# REACTIVITY OF INORGANIC PHOSPHORUS IN THE SPODIC HORIZON

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1997

To my eldest sister Ate Elvie, whose strength of character and spirit has been a constant source of inspiration, I dedicate this work.

ACKNOWLEDGMENTS

I would like to express my gratitude to a number of people who provided assistance and support throughout the course of my graduate program. I am indebted to Dr. D.A. Graetz, chairman of my supervisory committee, for giving me the opportunity to further my education here at the University of Florida. I am particularly thankful for the financial support I received in the form of a research assistantship which enabled me to continue my studies. Sincere thanks go to Drs. K.R. Reddy, R.D. Rhue, W.G. Harris, and G.R. Best for their time and assistance as members of my supervisory committee.

I am grateful to Vimala Nair for the interest she showed in my work and for the encouragement and moral support she unselfishly gave me when I needed them the most. Her insightful comments and suggestions during all phases of the study were extremely helpful in the completion of this work.

I truly appreciate the friendship of my fellow graduate students, Shailesh Patel and Len Scinto, with whom I shared many invaluable experiences in and out of the classroom. Their camaraderie and great sense of humor helped ease the heavy pressures of graduate work.

I owe much gratitude to my mother, brothers and sisters, and nieces and nephews for their love, encouragement, and understanding during this long process. Their pride in my work and accomplishments made earning this degree even more special.

And finally, I give my warmest thanks and appreciation to Candee Carigma whose love, patience, and understanding enabled me to see this work through to the very end. She was always there for me and never wavered in her support especially during the writing of this dissertation.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

# REACTIVITY OF INORGANIC PHOSPHORUS IN THE SPODIC HORIZON

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August 1997

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The reactivity of phosphorus (P) in the spodic (Bh) horizon has drawn increased attention in recent years, in large part due to the growing public concern over accelerated eutrophication of many lakes and streams. Considerable evidence exists that the Bh horizon can function as a sorption sink for P. However, the soil factors and environmental conditions under which P can be retained or released by the Bh horizon are not well understood. This research was conducted (i) to provide a quantitative description of the surface charge properties of Bh horizons from selected Florida Spodosols, (ii) to evaluate their P sorption and release properties under aerobic and anaerobic conditions, (iii) to determine the rate and extent of P sorption and desorption reactions in the Bh horizon as influenced by pH, and (iv) to study the effect of water table manipulations on P leaching from a Spodosol differentially impacted with animal wastes.

The Bh horizons exhibited charge properties similar to constant potential colloids, as both the sign and magnitude of the net charge varied with pH and ionic strength of the soil solution. The pH values at which the net surface charge underwent reversal (PZSE) ranged from 2.90 to 4.20. The soils exhibited positive and negative charges within the range of pH values studied. The pH values at which there was equal adsorption of cations and anions by the Bh horizon (PZNC) ranged from 2.60 to 4.90. Phosphorus loading increased the net negative charge of the soils.

The Bh horizons exhibited P sorption capacities that were consistent with their Al content. $CuCl_2$-extractable Al (Al associated with organic matter) was the single most important chemical property contributing to P sorption in these soils. Langmuir $S_{max}$ values ranged from 3.9 to 30.7 mmol P $kg^{-1}$. The effect of flooding on P sorption and desorption was generally small and inconsistent.

The Bh samples showed varying degrees of P sorption-desorption hysteresis. The observed "irreversibility" was most pronounced in high-Al soils, where over 70% of the added P remained in the adsorbed phase.

Sorption of P was characterized by an initially rapid reaction which became increasingly slow with time. The fast reaction was suggested to involve specific adsorption of P on amorphous Al oxides by a ligand exchange mechanism. The slow reaction, based on P solubility and fractionation data was postulated to involve formation of discrete Fe- and Al-P compounds.

Phosphorus sorption and desorption were influenced by pH. The reduction in P sorption with increasing pH was explained on the basis that as pH increases, the charge

on the amphoteric surfaces and their electrostatic potential decrease. Greater desorbability of P at high pH was ascribed to the lower bonding energy between sorbed P and oxide surfaces as their negative charge increases with increasing pH.

There is a great potential for surface water contamination with P from soils heavily impacted with animal wastes. With 60% of the total P in the labile pool, the soil from high manure-impacted areas would have approximately 3160 kg P $ha^{-1}$ in the surface layer that could potentially be available for transport. The Bh horizon under flooded and drained conditions provided limited storage for P moving from the surface layer.

# CHAPTER 1
# INTRODUCTION

Spodosols are the most extensive soils in Florida. These soils occur along the hydrologic continuum from terrestrial to wetlands and aquatic systems. Thus, the fate and transport of applied phosphorus (P) in these soils could determine to a large extent the amount of P that enters our rivers and lakes.

Spodosols are characterized by sandy textures, fluctuating water table, and the presence of a spodic horizon (Bh) below an A-E horizon sequence. The reactive component of a spodic horizon is principally an accumulation of amorphous mixtures of organic matter and aluminum (Al) (Soil Survey Staff, 1996). This characteristic composition coupled with a naturally acid soil reaction account for the propensity of the spodic horizon to adsorb P.

The chemistry of P in the spodic horizon has generated research interests in recent years (Burgoa, 1989; Mansell et al., 1992; Graetz and Nair, 1995), in large part due to the growing public concern over the accelerated eutrophication of many lakes and streams. The spodic horizon can function as a sink for P moving from the surface horizons (Hortenstine, 1978; Flaig et al., 1986; Burgoa et al., 1991; Nair et al., 1995, 1997). Presently, however, there is a general lack of understanding of the soil factors and environmental conditions under which the spodic horizon can either retain or supply P to

our water systems. Recognition of the role of the spodic horizon in P transport process under variable soil conditions will become increasingly important, as more and more of Florida's previously idle Spodosols are being developed for agricultural and non-agricultural purposes.

## Statement of the Problem

The role that soil plays in abating certain water quality problems has long been recognized. For many years, land application has been a well-established practice for disposing of industrial, municipal, and agricultural wastes (Sommers and Sutton, 1980). However, indiscriminate application of various wastes to soils beyond their carrying capacity could lead to accumulation and eventual transport of nutrients such as P and other contaminants to adjacent water bodies. Lake Okeechobee, for example, the major aquatic resource for water storage, wildlife, and recreation in south Florida has been reported to be on the verge of becoming hypereutrophic due to increased P loading (Bottcher et al., 1995). Extensive monitoring of the lake and its nutrient inputs revealed that the primary source of P to the lake was the dairy farming and beef cattle ranching north of the lake and the sugarcane and vegetable farming south of the lake (Bottcher et al., 1995). The dairies (approximately 35,000 head) were found to be the single most intensive source of P, accounting for about 49% of the total P input to the lake (Federico et al., 1981).

Transport of P from the dairy farms to receiving waters in the basin is exacerbated by unfavorable soil and hydrologic conditions (Allen, 1987). Efficient removal of P by

soil is dependent, among other factors, on its texture, pH, and mineral components (Syers and Iskandar, 1981). Most of the dairy sites in the watershed are located on Spodosols on a relatively level landscape. These soils consist of three primary horizons, namely, A, E, and Bh. The A horizon is sandy with small amounts of organic matter and generally has a depth of 15 to 20 cm. The E horizon located immediately below the A horizon is highly eluted with a thickness ranging from 20 to 140 cm depending on the soil type. Below the E horizon is the spodic horizon (Bh) in which amorphous mixtures of organic matter and Al, with or without iron (Fe), have accumulated. The spodic horizon is naturally acidic and has been shown to sorb P. However, as the water table rises to the surface during the rainy season, limited movement of P into the spodic horizon results in enhanced subsurface lateral P transport. Rapid immobilization of P is averted by the low P retention capacity in the A and E horizons, and the high water table which promotes surface runoff and lateral seepage (Allen, 1987; Capece, 1994). Movement of P into the spodic horizon is relatively unimpeded during dry months when water table is below the Bh horizon.

Nair et al. (1995) reported substantial accumulation of P from animal wastes in the spodic horizon over the years. Although P in the spodic horizon was largely Al- and Fe-bound, the large pool of labile P especially in the active-intensive dairy component indicates that potentially high levels of P could eventually find its way into the waterways. Thus, the question of whether the spodic horizon could serve as a source of or a sink for P is posed. Although spodic horizon is known to sorb P readily, its retention and release properties depend not only on their mineralogical and chemical composition

but also on an array of environmental conditions and physico-chemical processes governing P behavior. A prerequisite to understanding the role of spodic horizon in the overall P retention is an assessment of the interactions between P and soil constituents, and the mechanisms and processes that influence them.

## Need for Research

The Spodosols in south Florida are an important component of the Lake Okeechobee Basin, impacting both hydrology and water quality. Although considerable information is now available concerning the fate and transport of P in the Lake Okeechobee Basin, the currrent state of knowledge does not allow certain predictions of P loadings to the lake (Haan, 1995). Modeling P loading rates in runoff waters requires a description of the P retention processes in soils. Several processes may cause retention of P by soil constituents and control the release of P to runoff water. These processes include adsorption of P on mineral surfaces, precipitation of P-bearing mineral phases, immobilization by soil biota, mineralization of organic P, and ion exchange by positively charged soil colloids (Berkheiser et al., 1980). These, in turn, are influenced by pH, redox, organic matter content, mineral composition, and surface charge characteristics of the soil (Syers and Iskandar, 1981). Thus, an understanding of the behavior of P in the spodic horizon under changing soil conditions is imperative in defining its role in the overall transport process. Quantitative data on the chemistry of P in the spodic horizon remain meager. It is hoped that this study will generate information that will aid in

evaluating the lateral transport of P in Spodosols to drainage ways, and subsequently, to rivers and lakes.

## Objectives

The main objective of this study was to evaluate the reactivity of P in the spodic horizon of selected Florida Spodosols. The specific objectives were as follows: (i) to describe quantitatively the surface charge characteristics of the spodic horizons in relation to P sorption behavior, (ii) to evaluate the P sorption and release properties of the soils under aerobic and anaerobic conditions, (iii) to determine the rate of P sorption and desorption as influenced by pH, and (iv) to examine the effect of water table manipulations on P leaching from a Spodosol differentially impacted with animal wastes.

## Dissertation Format

The subsequent chapters in this dissertation are written as independent manuscripts intended for journal publication. Chapter 2 is a quantitative description of the electrochemical properties of the soils. The P sorption and desorption characteristics of the soils under aerobic and anaerobic conditions are examined in Chapter 3. Chapter 4 evaluates P sorption and desorption kinetics in soils as influenced by pH. The impact of water table depth on P leaching from a Spodosol loaded with dairy manure is addressed in Chapter 5. Overall summary and conclusions are discussed in Chapter 6.

# CHAPTER 2
# SURFACE CHARGE PROPERTIES OF SPODIC HORIZONS FROM SELECTED FLORIDA SPODOSOLS

## Introduction

The fate and transport of nutrients in the soil are dependent upon physico-chemical processes which occur at the soil solution-particle interface. The electrical charges on the surface of the colloidal particles influence these processes and are therefore important in studying nutrient behavior in soils. An understanding of surface charge is basic to explaining sorption mechanism in both natural and synthetic systems (Lewis-Russ, 1991). Ion retention depends directly on the sign and magnitude of charges associated with various soil components. The stability of soil aggregates and subsequent resistance to erosion or breakdown by dispersing agents are affected by whether the soil contains any amphoteric constituents and by the manner in which such constituents interact with one another (El Swaify, 1973). Surface charge properties have also been used as a tool for assessing pedogenic development (Hendershot and Lavkulich, 1978; Hunter and Busacca, 1987) and have important implications for soil fertility (Naidu et al., 1990) and environmental quality (Stumm, 1992).

On the basis of electrochemistry, soil colloids can be categorized into those with constant surface charge and those with constant surface potential (van Olphen, 1977). Colloids with constant surface charge include zeolites and expansible phyllosilicates such

as vermicullite and montmorillonite. These minerals derive their surface charge from isomorphous substitution in the interior of the crystal lattice. Commonly, $Al^{3+}$ substitutes for $Si^{4+}$ in the silica tetrahedral layers and $Mg^{2+}$ for $Fe^{3+}$ or $Al^{3+}$ in the alumina octahedral layers. The resulting charge imbalance is permanent and cannot be influenced by pH of the ambient solution. Structural charge on common layer-silicate minerals can vary from practically zero to >200 cmol $kg^{-1}$ (McBride, 1989). Colloids with constant surface potential are represented by amphoteric oxides and hydroxides, organic matter, and some 1:1 layer silicates such as kaolinite and halloysite. For oxide and hydroxide systems with completely reversible interfaces, the surface charge originates from the adsorption and desorption of potential determining ions, $H^+$ and $OH^-$. Negative charge generation in organic matter arises from the ionization of carboxyl, phenol, enol, and imide groups (Allison, 1973). Values reported for organic matter ranged from 30 to 300 cmol $kg^{-1}$ (Bell and Gillman, 1978). Constant potential systems are characterized by an equilibrium activity of the potential determining ions in solution at which the net surface charge is zero. This point is referred to as the point of zero charge (PZC) and is often found to be more or less characteristic of a given oxide or hydroxide. It is the most important parameter in a variable charge system because it determines the sign of the net surface charge (Uehara and Gillman, 1981). At pH values more acid than the PZC, the net charge will be positive, while at pH values more alkaline than the PZC, the net surface charge will be negative.

The nature and magnitude of surface charge in highly weathered and volcanic ash soils have been investigated quite extensively since the early seventies. The work of van

Raij and Peech (1972) provided the foundation for recent advances in the electrochemistry of variable charge soils. Their studies involving two highly weathered Oxisols and an Alfisol from Brazil, showed that the electrochemical behavior of these soils was similar to those of metallic oxides and hydroxides, one which could be adequately predicted by theoretical models. Subsequent studies on similar groups of soils (Keng, 1974; Keng and Uehara, 1975; El-Swaify and Sayegh, 1975; Espinoza et al., 1975; Madrid et al., 1980; Manrique, 1985; Marcaño-Martinez and McBride, 1989; Bleeker and Sageman, 1990) showed that in many cases, the soils could be treated as constant surface potential systems.

In the United States and other temperate regions of the world, the interest in the study of variable charge soils center around Spodosols. Also referred to as Podzols, these soils are characterized by relatively high accumulations of Fe and Al oxides along with organic matter in the spodic horizon. Selective chemical dissolution studies and spectroscopic examinations (McKeague and Day, 1966, 1969; Higashi et al., 1981; Farmer et al., 1983; Wang et al., 1987; Kodama and Wang, 1989; Gustafsson et al., 1995) have shown that a considerable proportion of the Fe and Al oxides in the spodic horizon exist in amorphous (noncrystalline) inorganic and organic-bound forms. The presence of hydrated aluminosilicates of short-range order such as allophane and imogolite has also been reported for Spodosols in Canada (Brydon and Shimoda, 1972) and for Podzols and Brown Forest soils in Scotland (Tait et al., 1978). This characteristic composition causes the cation exchange capacity (CEC) of the spodic horizons to be highly pH dependent. Thus, it would seem likely that spodic horizons may exhibit amphoteric charge

properties--a phenomenon previously thought to occur only in highly weathered soils and soils derived from volcanic ash. Electrochemical studies involving spodic horizons were limited to those found in regions of cooler climates (Clark et al., 1967; Laverdiere and Weaver, 1977; Laverdiere, 1982; Polubesova et al., 1995). Virtually no studies of this nature have been conducted on spodic horizons from the coastal plain of the southeastern United States. Hence, the objectives of this study were (i) to examine the surface charge characteristics of spodic horizons from across the state of Florida, (ii) to evaluate the effect of P addition on surface charge, and (iii) to assess the environmental implications of P loading on the charge properties. The surface charge properties of the spodic horizons would be a function of the form and amount of metallic oxides and hydroxides they contain. Aluminum and Fe oxides in pure form have relatively high PZC values, usually between pH 7 and pH 9 depending on their composition and crystallinity. Thus, the soil whose colloidal fraction is dominated by these oxides was hypothesized to exhibit the highest PZC under natural conditions.

## Theoretical Considerations on Surface Charge Properties of Soils

### Operational Definitions

The study of electrochemical properties of variable charge systems is a relatively young field. Although certain principles have emerged in recent years, the fine details which allow quantitative ion exchange prediction are still lacking. Currently, there is a great deal of confusion in terminology, emanating in part from the lack of uniformity in the charge measurement techniques, and in part from the theoretical models used to describe the phenomena that occur at an electrically charged solid-liquid interface

(Lewis-Russ, 1991). Indeed, the vast array of electrochemical terms used in the literature is not only technique dependent but also model specific.

Ion exchange properties in soils result from an excess of charges at the surface of the colloids which must be balanced by oppositely charged counterions to maintain the electroneutrality of the system. As mentioned earlier, the surface charge of a colloid can result from structural factors inherent in the mineral or from adsorption of potential determining ions (PDIs). PDIs are ions that are common to both the mineral and the solution, and determine charge by adsorption and desorption (Arnold, 1978). For metallic oxides and hydroxides, $H^+$ and $OH^-$ act as PDIs. Surface charge originating from internal crystal substitutions is permanent ($\sigma_p$) and cannot be influenced by changes in pH of the ambient solution. Surface charge resulting from the adsorption of potential determining ions is termed variable ($\sigma_v$) because it changes with pH and ionic strength of the ambient solution (White and Zelazny, 1986). For soils containing both permanent and variable charge, values for cation exchange capacity (CEC) and anion exchange capacity (AEC) can be equal at some particular pH value. This pH corresponds to the point of zero net charge (PZNC) ( Parker et al., 1979). For variable charge systems, there is a pH at which the net surface charge resulting from the adsorption of the potential determining ions $H^+$ and $OH^-$ is zero. This pH value is referred to as the point of zero charge (PZC). At this pH, the protonation and deprotonation of surface hydroxylated groups are equal, and it is the point of intersection of potentiometric titration curves at different electrolyte concentrations (Uehara and Gillman, 1980a). The equilibrium pH attained between a solid and solution before acid or base additions is called the zero point of titration (ZPT).

As the procedure suggests, PZC has also been termed the point of zero salt effect (PZSE) (Parker et al., 1979; Sposito, 1981), the crossover point, or the isoelectric point (IEP) (Pyman et al., 1979). PZC is the same as PZSE when no specific adsorption of ions other than $H^+$ and $OH^-$ has occurred (Sposito, 1984). Specific adsorption refers to the inner-sphere complexes formed between surface functional groups on soil minerals and ions in the soil solution (Sposito, 1981). Bowden et al. (1979) proposed the pristine point of zero charge (PPZC) term for the unique case where PZC=IEP. In a pure variable charge system, the PZC, IEP, and ZPT occur at the same pH value. In a system containing permanent charge, the measured PZC will be different from the IEP of the variable charge system and the crossover point will be displaced above or below the ZPT by an amount equal to the permanent charge (Hendershot and Lavkulich, 1978).

Theoretical Models Used to Describe Surface Charge

While it may be true for some extreme cases, most soils do not have purely permanent or purely variable charge systems. Generally, all soils contain a mixture of both constant and variable charge surfaces in various proportions. It is difficult to separate soil colloids into constant surface charge and constant surface potential because a single mineral can exhibit both types. For example, soils in temperate regions tend to be dominated by the constant charge minerals; however, their edge surfaces and oxide-organic matter coatings generally carry a pH-dependent charge (White and Zelazny, 1986). But since the interpretation of data for soil management purposes depends on the knowledge of surface characteristics of the soil as a whole, it is imperative to partition the effect of the permanent and variable charge components on soil behavior.

The Gouy-Chapman model. Separation of the minerals into constant surface charge and constant surface potential type begins with the Gouy-Chapman double layer equation.

$$\sigma_o = (2c\epsilon RT/\pi)^{1/2} \sinh (zF\psi_o/2RT) \qquad (2\text{-}1)$$

where
$\sigma_o$ = Surface charge density, C $m^{-2}$
c = Electrolyte concentration, kmol $m^{-3}$
$\epsilon$ = Dielectric constant, 8.9 x $10^{-9}$ $C^2$ $J^{-1}$ $m^{-1}$
R = Gas constant, 8.314 x $10^3$ J $kmol^{-1}$ $K^{-1}$
T = Absolute temperature, 298°K
z = Ionic valence
F = Faraday constant, 9.6487 x $10^7$ C $kmol^{-1}$
$\psi_o$ = Surface potential, volts

For constant surface charge systems whose surface charge is controlled by lattice defects in the interior of the crystal, the double layer potential, the electrolyte concentration, and counterion valence do not influence the sign or magnitude of the surface charge. Thus, equation 2-1 takes the form

$$\text{constant} = (2c\epsilon RT/\pi)^{1/2} \sinh (zF\psi_o/2RT) \qquad (2\text{-}2)$$

An increase in either electrolyte concentration, valence or dielectric constant of the medium should result in a reduction in surface potential--a condition which can be attained by compressing the double layer.

For constant surface potential colloids whose charge is generated by the adsorption of potential determining ions, $H^+$ and $OH^-$, the surface potential $\psi_o$ can be held constant by maintaining pH constant. Equation 2-1 therefore takes the form

$$\sigma_o = (2c\epsilon RT/\pi)^{1/2} \sinh (zF/2RT) \text{ (constant)} \qquad (2\text{-}3)$$

Thus, an increase in the electrolyte concentration or valence, or the dielectric constant should result in a concomitant increase in surface charge.

The surface potential $\psi_o$ represents the difference in potential across the double layer formed by the reversible transfer of potential determining ions, $H^+$ and $OH^-$, and is given by a Nernst type equation

$$\psi_o = RT/zF \ln (C/C_o) \qquad (2\text{-}4)$$

where C is the concentration of PDI and $C_o$ is the concentration of PDI when $\psi_o = 0$.

For simple metal oxides and hydroxides for which $H^+$ and $OH^-$ act as PDI, Equation 2-4 can be rewritten as

$$\psi_o = 59 (pH_{PZC} - pH) \text{ mV at } 25°C \qquad (2\text{-}5)$$

where $pH_{PZC}$ is the pH at which $\psi_o = 0$.

Equations 2-1 through 2-5 describe the effects of pH and ionic strength variations on the electrochemical properties of constant potential colloids. That is, at pH values more alkaline than the PZC, the net charge will be negative while at pH values more acid than the PZC, the net charge will be positive. Furthermore, it can be seen that the magnitude of the net charge should increase with increasing electrolyte concentration. When the pH is equal to the PZC, the net charge will be zero and will be independent of the electrolyte concentration.

The Gouy-Chapman model presents, however, a serious limitation in that, even at moderately high surface potentials ($\psi_o \geq 100$ mV), unrealistically high values are predicted for the amount of counterions adsorbed into the diffuse layer. This is because

the Gouy-Chapman equation which treats ions as point charges does not take into account the actual size of the ions.

The Stern theory. In the Stern model, the finite size of the ions is taken into account. The surface charge is now assumed to be balanced by the charge in solution which is distributed between two layers. The charge in the layer close to the surface (adsorbed ions), called the Stern layer, is represented by $\sigma_1$. The charge in the other layer of ions (diffuse layer) is represented by $\sigma_2$. Thus the total charge $\sigma_o$ in both layers is,

$$\sigma_o = -(\sigma_1 + \sigma_2) \qquad (2\text{-}6)$$

The charge in the Stern layer is given by

$$\sigma_1 = N_i zF/(1 + N_A \rho/Mc) \exp[-(zF\psi_d + \phi)/RT] \qquad (2\text{-}7)$$

where $\sigma_1$ = Stern layer charge, C $m^{-2}$
$N_i$ = Number of adsorption sites available per $m^2$ of surface to ionic species i.
$N_A$ = Avogadro's number, 6.023 x $10^{23}$
M = Molar mass of the solvent, kg
$\rho$ = Solvent density, kg $m^{-3}$
c = Electrolyte concentration, kmol $m^{-3}$
$\phi$ = Specific adsorption potential, J
$\psi_d$ = Stern potential, volts
d = Thickness of Stern layer, m

The charge in the diffuse layer is given by the Gouy-Chapman equation, but now the reference is the Stern potential instead of the surface potential.

$$\sigma_2 = (2c\epsilon RT/\pi)^{1/2} \sinh (zF\psi_d/2RT) \qquad (2\text{-}8)$$

The surface charge is also given by the equation for a molecular condenser,

$$\sigma_o = (\epsilon'/4\pi d)(\psi_o - \psi_d) \qquad (2\text{-}9)$$

where $\epsilon'$ is the average dielectric constant of the Stern layer and d is the thickness of the Stern layer. Although $\epsilon'$ and d are not determinable quantities, van Raij and Peech

(1972) were able to calculate the net surface charge by introducing reasonable values for these parameters which can be adjusted by experimental observations.

Other models. In addition to the Gouy-Chapman double layer model and its extension by Stern, several other mathematical models have been used to describe the boundary between the colloid with its adsorbed ions and the solution. There is the three-layer model that allocates ions near the surface to three distinct planes. The innermost layer contains adsorbed $H^+$ and $OH^-$ which experience the surface potential and are responsible for the surface charge (Davis et al., 1978; James and Parks, 1982). There also is the four-layer model that allocates an additional layer for specifically adsorbed ions, such as phosphate and copper (Bowden et al., 1980). Detailed descriptions of these models are given by Westall and Hohl (1980) and Barrow (1985).

Techniques for Measuring Surface Charge in Soils

As alluded to earlier, much of the confusion in the study of the chemistry of variable charge soils is related to the different procedures used for measuring surface charge and the assumptions needed for data interpretation. Several procedures have been developed for measuring surface charge properties of pure and mixed systems. Two of the most commonly used techniques are potentiometric titrations and ion adsorption. Potentiometric titration involves the measurement of the net adsorption of $H^+$ and $OH^-$ at different pH values and at different ionic strengths. Because of the characteristics of amphoteric surfaces, there is a pH at which the different curves intersect, i.e., a point at which adsorption of protons is independent of ionic strength. This term as defined earlier is the point of zero salt effect (PZSE). If the electrolyte is assumed to have no effect on

surface charge, PZSE will occur at the same pH as PZC (Lewis-Russ, 1991). At pH values above the PZSE, the surface charge is negative, and below the PZSE the surface charge is positive. Potentiometric titration is rapid, but the method is often criticized for overestimating changes in surface charge with pH. The error is largely due to the consumption of $H^+$ and $OH^-$ by surface reactions as well as those associated with the dissolution of the soil and hydrolysis of ions in solution (Duquette and Hendershot, 1993a). To account for this error, the same authors developed a modification of the backtitration technique--a method first introduced by Schulthess and Sparks (1986, 1988) for the evaluation of the surface charge of oxides. The advantage of this method is that it takes into account the dissolution of the solid phase and that the surface charge measured as a function of pH is represented by a series of inflection points and plateaus that can be associated with different surface reactions. The different constants derived from the inflection points and plateaus were related to the soil constituents occurring mainly as surface coatings on the soil particles. CEC values reported for backtitration were in close agreement with those obtained from ion adsorption (Schulthess and Sparks, 1988; Duquette and Hendershot, 1993b).

Ion adsorption technique (Schofield, 1949) involves the measurement of retention of an indifferent ion (adsorbed onto the surfaces by electrostatic attraction), such as $Na^+$, $K^+$, $NO_3^-$, and $Cl^-$ as a function of pH at a fixed ionic strength. This method provides an estimate of the cation exchange capacity (CEC) and anion exchange capacity (AEC), as well as the net charge (AEC-CEC) at each pH and is considered to measure the point of zero net charge (PZNC). The success of the ion adsorption technique depends on

choosing the appropriate electrolyte that will replace all surface-adsorbed ions without forming charged inner-sphere surface complexes (Sposito, 1981,1984). Different electrolytes will result in different values for the surface charge. If the electrolyte and experimental conditions are similar to the natural setting, the resulting surface charge will be of practical use, even though it may not be the optimal value (Sposito, 1984). Ion adsorption provides a fairly accurate measure of AEC and CEC, but the procedure is tedious and time consuming. Lewis-Russ (1991) discussed the merits and drawbacks of the different techniques currently employed in electrochemical studies, including electrophoretic mobility, salt titration, and mineral addition.

## Materials and Methods

### Selection and Description of Soils

Samples from spodic horizons representing sixteen Spodosols from fourteen Florida counties were used in the study (Fig. 2-1). Sample selection was based primarily on the total contents of Fe and Al in the spodic horizon and the relative extent of occurrence of the soil series to which the samples belong. Samples were selected to cover the wide range of Al and Fe levels commonly found in Florida Spodosols. The selection process was aided by the use of an electronic database called RAMIS which is a compilation of the characterization data for Florida soils. The program was developed jointly by the University of Florida Soil and Water Science Department and the USDA Soil Conservation Service as part of the Florida Cooperative Soil Survey program. The soils were selected from a host of samples that had been archived up to 15 years (Harris et

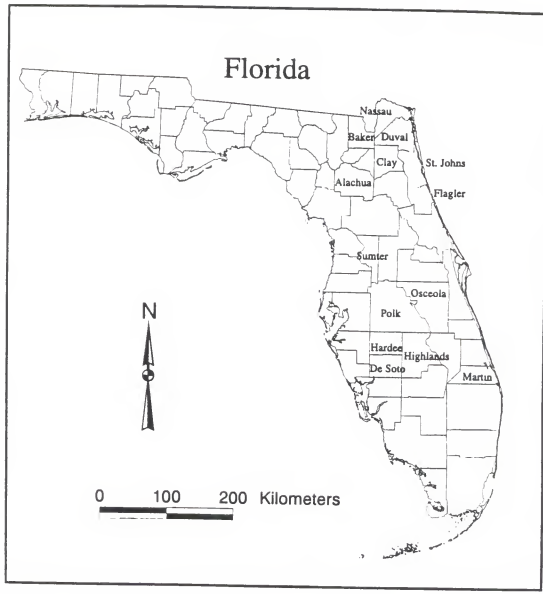



Fig. 2-1. Location of the spodic samples used in this study.

al., 1996). Once the final selection was made, aliquots of stored samples were obtained from the archive. Fresh samples of EauGallie and Wauchula soils were taken for use in other detailed studies that will be discussed later. Soil samples were air-dried and sieved to pass through a 2-mm sieve.

Of the sixteen samples, thirteen were Alaquods; the other three were Haplorthods (Table 2-1). Alaquods are characterized by a fluctuating water table and a spodic horizon that is principally an accumulation of Al and organic matter. These soils are most common on the coastal plains of the southeastern United States, particularly in Florida. Haplorthods are the more or less freely drained Spodosols in which Fe, organic matter, and Al have accumulated (Soil Survey Staff, 1996). The location of the spodic horizons varied greatly, ranging from a shallow 23 cm to as deep as 203 cm. The colloidal fraction in the samples ranged from 1.6 to 9.9% and was dominated by quartz mineralogy. Secondary minerals such as montmorillonite, kaolinite, and hydroxy-interlayered vermicullite were found in variably low amounts in most soils.

Soil Characterization

The soils were initially analyzed for selected chemical properties. All analyses were carried out in triplicate. Soil reaction (pH) was determined in water and 1M KCl using a 1:1 soil:solution ratio (McLean, 1982). Organic carbon was determined by rapid oxidation with a hot mixture of $K_2Cr_2O_7$ and $H_2SO_4$ (Nelson and Sommers, 1982). Exchangeable Ca, Mg, K, and Na were extracted from a 0.1M $BaCl_2$ solution following a 2-hour equilibration (Gillman, 1979). Exchangeable Al was determined by extraction

Table 2-1. Location, mineralogy, and taxonomic classification of the spodic horizons used in the study. Data were obtained from soil survey reports prepared jointly by the University of Florida Soil and Water Science Department and the USDA Soil Conservation Service.

| Soil Series | County | Depth, cm | Clay, % | Mineralogy[1] | Taxonomic Group |
|---|---|---|---|---|---|
| Cornelia | Duval | 99-112 | 9.9 | MT>QZ>>KL>HIV | Arenic Haplorthods |
| EauGallie | Highlands | 66-84 | 4.7 | QZ>MT>>KL | Alfic Arenic Alaquods |
| Immokalee | Flagler | 109-137 | 2.4 | KL>QZ>HIV | Aeric Alaquods |
| Kingsferry | Nassau | 170-203 | 2.2 | QZ>>>KL>HIV | Arenic Alaquods |
| Leon | Baker | 43-58 | 5.0 | No Data | Aeric Alaquods |
| Myakka | Sumter | 64-79 | 1.7 | QZ>HIV>KL>MT | Aeric Alaquods |
| Narcoose | Polk | 43-48 | 3.3 | QZ>>MT>HIV>KL | Entic Haplorthods |
| Oldsmar | Highlands | 89-109 | 3.4 | QZ>>MT>KL>HIV | Alfic Arenic Alaquods |
| Ona | Hardee | 23-41 | 5.1 | QZ | Arenic Alaquods |
| Pomello | St. Johns | 114-130 | 3.6 | QZ | Arenic Haplorthods |
| Pomona | St. Johns | 55-58 | 3.9 | QZ>>HIV>>KL | Ultic Alaquods |
| Sapelo | Clay | 46-58 | 4.0 | QZ>HIV>>KL | Ultic Alaquods |
| Smyrna | Desoto | 188-203 | 1.6 | QZ>>MT>HIV>KL | Aeric Alaquods |
| Vero | Osceola | 61-71 | 6.0 | QZ>>>MT>HIV>FD>KL | Alfic Alaquods |
| Wabasso | Martin | 58-91 | 2.0 | QZ>>>MT>KL | Alfic Alaquods |
| Wauchula | Alachua | 46-58 | 7.3 | QZ>>>HIV>KL | Ultic Alaquods |

[1]Arranged in relative order of abundance.

MT-montmorillonite; HIV-hydroxy interlayered vermicullite; KL-kaolinite; QZ-quartz; FD-feldspar.

with 1M KCl (Barnhisel and Bertsch, 1982). The sum of exchangeable cations and Al was taken to represent the effective cation exchange capacity of the soil (ECEC) (Juo et al., 1976).

The different forms of Fe and Al in the soils were determined by selective dissolution. Aluminum and Fe associated with the organic matter were extracted with 0.1M $Na_4P_2O_7$ (Wada and Higashi, 1976). The amorphous forms of Al and Fe were dissolved in acidified 0.2M $(NH_4)_2C_2O_4$ (McKeague and Day, 1966). The citrate-dithionite-bicarbonate method of Mehra and Jackson (1960) was used to extract the crystalline forms of Al and Fe in the soils. The extracts were analyzed for Al and Fe using an ICAP emission spectrophotometer.

The elemental concentrations of Al, Fe, Si, and P were determined by digesting a finely ground sample in nitric-perchloric acid mixture (Olsen and Sommers, 1982). Similarly, the analysis of Al, Fe, Si, and P in the digestate was done by ICAP emission spectrophotometry.

Measurement of Surface Charge

The potentiometric titration and the ion adsorption methods were used in the characterization of the surface charge as a function of pH and electrolyte concentration. Although often criticized for problems in execution and interpretation, they remain the most commonly used techniques for studying charge characteristics for amphoteric surfaces (Lewis-Russ, 1991).

Potentiometric titrations. Potentiometric titration curves for the samples were obtained using the method of van Raij and Peech (1972). Four-gram samples were

suspended in 10 mL of 2.0, 0.2, 0.02, and 0.002M NaCl to which known quantities of 0.1M HCl or 0.1M NaOH were added to obtain a certain pH range. The final volume was brought to 20 mL with deionized water to give final NaCl concentrations of 1.0, 0.1, 0.01, and 0.001M. The suspensions were equilibrated at room temperature in capped 50-mL centrifuge tubes and shaken twice daily over a 3-day period. The pH of the suspensions was then taken and titration curves were constructed. The amount of $H^+$ or $OH^-$ adsorbed by the soil at a given pH was estimated by taking the difference between the amount of acid or base added to the suspension and the amount of acid or base required to bring a blank solution of the same volume and same concentration of NaCl solution, without the soil sample, to the same pH. The point at which the titration curves intersect is the PZSE.

Ion adsorption. The distribution of positive and negative charges in the soil samples as a function of pH in 0.01M NaCl was determined using a modification of the method developed by Schofield (1949). Sodium chloride was used as the swamping electrolyte with the assumption that the colloidal fraction of the soils contained no sites capable of specifically adsorbing $Na^+$, and thus, NaCl could be treated as an indifferent electrolyte. Four-gram air-dried samples were placed in each of the twelve 30-mL preweighed centrifuge tubes. In order to eliminate problems that may result from high levels of soluble Al in the soil, the samples were successively washed once with 1M NaCl, twice with 0.1M NaCl, and thrice with 0.01M NaCl. Washings were done by shaking the suspensions for 1 hour followed by centrifugation at 3620 *g* for 10 minutes. The supernatant was carefully removed with a syringe to avoid loss of clay. Varying amounts of 0.1M HCl or 0.1M NaOH were added to the tubes along with 20 mL of

0.02M NaCl. Known quantities of deionized water were added to the tubes such that the final concentration of NaCl was 0.01M. The samples were equilibrated at room temperature with intermittent shaking in an end-over-end shaker for 3 days. The samples were then centrifuged and the supernatant solutions saved for pH, $Na^+$, and $Cl^-$ determinations. Because KCl often leaks from a pH electrode during measurement, 10-mL solution aliquots were reserved for $Cl^-$ analysis prior to pH measurements (Anderson and Sposito, 1992). The tubes were then immediately capped and weighed to estimate the entrained NaCl. Adsorbed and entrained $Na^+$ and $Cl^-$ were displaced by washing the soil five times with 20 mL of 0.5M $NH_4NO_3$. Sodium was determined with a flame photometer and Cl by coulometric-amperometric titration with silver ions (Cotlove et al., 1958). The amounts of $Na^+$ and $Cl^-$ displaced after correction for the entrained NaCl within the soil volume, were used as estimates of the negative and positive charges, respectively.

Pre-treatment of Soils with Phosphorus

The influence of P addition on PZC and charge characteristics was evaluated on EauGallie and Wauchula soils. These soils were pre-selected based on their initial Fe and Al contents. Wauchula represented the high Al, low Fe-containing soils while EauGallie represented the soils that were low in both elements. Solution P (as $KH_2PO_4$) was added to soils at levels equivalent approximately to 0, 1/2, 1, and 2 times their P sorption maximum ($S_{max}$) estimated from the linear form of the Langmuir equation. EauGallie was treated with 0 to 23.7 mmol P $kg^{-1}$ and Wauchula with 0 to 61.3 mmol P $kg^{-1}$. The samples were equilibrated aerobically at room temperature for 28 days in small plastic

bags at a moisture level equivalent to field capacity. The moisture content of the soils was maintained by adding appropriate amounts of deionized water twice a week. After incubation, the soils were air-dried and sieved through a 2-mm sieve. Potentiometric titration and ion adsorption curves were established for these soils using the procedures described earlier.

## Results and Discussion

### Initial Chemical Properties

The soils in general were very acidic (Table 2-2). Soil pH values in 1M KCl were lower than those measured in water indicating that all soils at their natural pHs are negatively charged. High exchangeable Al concentrations were associated with low pH and low exchangeable bases, and vice versa. Summation of exchangeable bases gave values ranging from 1.52 to 102.97 $mmol_{(+)}kg^{-1}$. Except for Cornelia, Ona, Vero, and Wabasso, all soils had exchangeable Al greater than exchangeable bases combined. The soils had very low capacity to retain cations under field conditions. The average effective CEC of the soils excluding Vero soil was 2.08 $cmol_{(+)}kg^{-1}$. This is not difficult to understand considering the soils are predominantly sand. Organic carbon content of the soils varied from 7.3 to 32.6 g $kg^{-1}$. These values were comparable to those reported for spodic horizons of soils from New York and Canada (Laverdiere and Weaver, 1977). Except for Vero, the soils were dominated by Al. The mole ratio of Al to Fe ranged from 1.2 to 42.7. Average Al and Fe contents of the soils were 152.9 and 15.5 mmol $kg^{-1}$,

Table 2-2. Selected chemical properties of the spodic horizons used in the study.

| Soil Series | $pH_{H2O}$ | $pH_{KCl}$ | Exchangeable Bases, $mmol_{(+)}\ kg^{-1}$ | | | | | Exch. Al $mmol_{(+)}\ kg^{-1}$ | ECEC¶ $cmol_{(+)}\ kg^{-1}$ | Org. C $g\ kg^{-1}$ | Total, $mmol\ kg^{-1}$ | | | | Al:Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ca | Mg | K | Na | Σ Bases | | | | Al | Fe | Si | P | |
| Cornelia | 4.07 | 3.15 | 8.25 | 2.33 | 0.38 | 1.29 | 12.25 | 11.94 | 2.42 | 13.2 | 139.27 | 65.58 | 10.5 | 36.29 | 2.12 |
| EauGallie | 4.29 | 3.42 | 1.92 | 2.84 | 0.28 | 0.74 | 5.78 | 17.03 | 2.28 | 14.9 | 32.15 | 16.04 | 1.66 | 1.40 | 2.00 |
| Immokalee | 5.34 | 4.39 | 0.81 | 1.34 | 0.26 | 0.54 | 2.95 | 22.63 | 2.56 | 20.4 | 47.54 | 2.40 | 1.90 | 2.04 | 19.80 |
| Kingsferry | 4.33 | 3.98 | 0.40 | 0.51 | 0.26 | 0.35 | 1.52 | 6.10 | 0.76 | 32.1 | 465.68 | 13.66 | 5.17 | 8.18 | 34.09 |
| Leon | 4.11 | 3.54 | 1.38 | 0.67 | 0.31 | 0.52 | 2.88 | 18.96 | 2.19 | 21.1 | 139.33 | 3.67 | 1.19 | 3.03 | 37.96 |
| Myakka | 4.11 | 3.15 | 1.67 | 1.45 | 0.32 | 0.47 | 3.91 | 17.59 | 2.15 | 24.7 | 83.28 | 3.81 | 2.25 | 4.08 | 21.86 |
| Narcoose | 4.23 | 3.17 | 1.19 | 2.88 | 1.56 | 1.04 | 6.67 | 6.74 | 1.34 | 14.4 | 94.02 | 3.94 | 1.31 | 9.27 | 23.86 |
| Oldsmar | 3.96 | 2.99 | 1.11 | 1.57 | 0.28 | 0.55 | 3.51 | 13.93 | 1.74 | 32.6 | 119.99 | 4.08 | 1.19 | 3.57 | 29.41 |
| Ona | 4.86 | 3.86 | 25.49 | 6.38 | 6.32 | 0.42 | 38.61 | 3.93 | 4.25 | 26.1 | 248.81 | 6.74 | 1.08 | 70.98 | 36.92 |
| Pomello | 4.20 | 3.42 | 0.62 | 0.67 | 0.28 | 0.38 | 1.95 | 9.07 | 1.10 | 15.3 | 53.76 | 1.26 | 0.71 | 1.83 | 42.67 |
| Pomona | 4.37 | 3.83 | 1.12 | 0.85 | 0.29 | 0.57 | 2.83 | 16.73 | 1.96 | 25.1 | 381.14 | 18.43 | 6.15 | 3.83 | 20.68 |
| Sapelo | 3.62 | 3.33 | 1.08 | 0.84 | 0.29 | 0.43 | 2.64 | 21.81 | 2.44 | 16.2 | 85.92 | 4.62 | 0.83 | 1.94 | 18.60 |
| Smyrna | 4.62 | 4.34 | 1.09 | 1.14 | 0.26 | 0.50 | 2.99 | 4.58 | 0.76 | 7.3 | 260.97 | 6.67 | 4.87 | 10.47 | 39.13 |
| Vero | 6.29 | 5.46 | 35.71 | 44.19 | 0.98 | 22.09 | 102.97 | 0.19 | 10.31 | 15.1 | 67.03 | 75.86 | 4.52 | 2.16 | 0.88 |
| Wabasso | 5.23 | 4.48 | 21.40 | 4.06 | 0.28 | 2.20 | 27.94 | 0.85 | 2.88 | 8.6 | 19.39 | 16.72 | 1.66 | 0.65 | 1.16 |
| Wauchula | 4.57 | 3.82 | 1.70 | 0.67 | 0.28 | 0.44 | 3.09 | 21.37 | 2.45 | 19.9 | 208.67 | 4.84 | 2.77 | 2.51 | 43.11 |

¶ ECEC- effective cation exchange capacity.

respectively. Concentrations of total P in the soils varied widely but were generally low. Values ranged from 0.65 mmol $kg^{-1}$ for Wabasso to as high as 71 mmol $kg^{-1}$ for Ona.

On a whole soil basis, the amounts of Al and Fe determined from selective dissolution were low (Table 2-3). These values would translate into astronomically high numbers if expressed as a fraction of the total clay content of the soils. Aluminum and Fe in the spodic horizons were largely amorphous [$(Al+Fe)_o$] comprising a combined average of over 60% of the total Al and Fe. Organically bound Al and Fe [$(Al+Fe)_p$] were similarly high. This was expected considering that organo-metallic complexes are an important component of the spodic horizon. Although the values obtained from CDB extraction [$(Al+Fe)_d$] appear as large as oxalate, this is somewhat misleading. The CDB reagent is considered to be less selective than acid oxalate reagent. It solubilizes a large portion of both crystalline and amorphous forms of Al and Fe. Thus, to obtain a realistic estimate of the amount of crystalline forms of Al and Fe in the soil, the convention is to take the difference between CDB and oxalate extractions (Freese et al., 1992). Compared to oxalate and pyrophosphate extractable Al and Fe, this fraction accounted for a very small portion of the total Al and Fe in the soils. The difference between CDB and oxalate-extractable Fe ($Fe_d$-$Fe_o$) has been used as a quantitative estimate of Fe in goethite and hematite (Parfitt and Childs, 1988). Relative to the total Fe content of the soils, this crystalline form of Fe in the soils was low, except for the Fe-dominated Vero soil.

Surface Charge Characteristics

Delta pH (ΔpH). A simple technique to determine whether a soil has a net positive or net negative charge is to measure the pH of the soil in water and a strong

Table 2-3. Forms of Al and Fe in the spodic horizons. (p is sodium pyrophosphate; o is ammonium oxalate; d is citrate-dithionite-bicarbonate).

| Soil Series | Extractable Al , mmol kg$^{-1}$ | | | Extractable Fe , mmol kg$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $Al_p$ | $Al_o$ | $Al_d$ | $Fe_p$ | $Fe_o$ | $Fe_d$ | $(Al+Fe)_p$ | $(Al+Fe)_o$[¶] | $Fe_d$-$Fe_o$[§] |
| Cornelia | 53.26 | 52.49 | 56.36 | 38.09 | 49.74 | 56.56 | 91.35 | 102.23 (50) | 6.82 |
| EauGallie | 22.06 | 23.74 | 24.97 | 12.20 | 15.25 | 15.35 | 34.26 | 39.09 (81) | 0.10 |
| Immokalee | 40.00 | 38.65 | 46.72 | 0.26 | 0.14 | 0.81 | 40.26 | 38.79 (78) | 0.67 |
| Kingsferry | 354.96 | 337.56 | 254.96 | 1.19 | 0.22 | 0.70 | 356.15 | 337.78 (70) | 0.48 |
| Leon | 75.91 | 82.16 | 99.98 | 0.58 | 0.66 | 0.96 | 76.49 | 82.82 (58) | 0.30 |
| Myakka | 56.45 | 50.35 | 57.88 | 1.00 | 0.68 | 1.12 | 57.45 | 51.03 (59) | 0.44 |
| Narcoose | 44.44 | 44.18 | 55.90 | 1.27 | 1.31 | 1.65 | 45.71 | 45.49 (46) | 0.34 |
| Oldsmar | 71.75 | 68.67 | 88.62 | 1.18 | 1.01 | 1.24 | 72.93 | 69.68 (56) | 0.23 |
| Ona | 166.80 | 168.59 | 223.63 | 2.95 | 3.14 | 4.93 | 169.75 | 171.73 (67) | 1.79 |
| Pomello | 42.90 | 46.02 | 48.57 | 0.21 | 0.20 | 0.38 | 43.11 | 46.22 (84) | 0.18 |
| Pomona | 265.61 | 258.48 | 265.51 | 5.81 | 3.11 | 5.79 | 271.42 | 261.59 (65) | 2.68 |
| Sapelo | 44.12 | 44.40 | 52.57 | 1.39 | 1.52 | 1.61 | 45.51 | 45.92 (51) | 0.09 |
| Smyrna | 180.61 | 153.67 | 133.13 | 2.19 | 0.72 | 1.19 | 182.80 | 154.39 (58) | 0.47 |
| Vero | 24.02 | 20.39 | 41.19 | 18.18 | 11.84 | 72.07 | 42.20 | 32.23 (23) | 60.23 |
| Wabasso | 13.91 | 13.34 | 12.85 | 13.63 | 12.87 | 16.66 | 27.54 | 26.21 (73) | 3.79 |
| Wauchula | 167.89 | 161.55 | 168.68 | 1.81 | 1.43 | 2.17 | 169.70 | 162.98 (76) | 0.74 |

[¶] Values in parentheses are $(Al+Fe)_o$ expressed as percent of total (Al+Fe).

[§] Estimate of Fe in goethite and hematite.

electrolyte solution such as 1M KCl (Mekaru and Uehara, 1972). The sign of the net charge of the soil is given by the expression

$$\Delta pH = pH_{KCl} - pH_{H2O}$$

As a rule, soils containing constant surface charge minerals should give -ΔpH values, as such colloids almost always carry a net negative charge. On the other hand, soils dominated by constant surface potential colloids can exhibit negative, zero, or positive ΔpH values depending on net surface charge. Delta pH values for the soils in this study are given in Table 2-4. The soils at their natural pH bore a net negative charge with ΔpH values ranging from -0.28 to -1.06. Delta pH values correlated significantly with the net surface charge of the soils ($r=0.532$, $p<0.05$) but not with the permanent and variable components of the surface charge. According to Uehara and Gillman (1981), a large negative ΔpH value indicates a high negative surface charge density but it does not indicate whether the charge is permanent or variable. However, the positive correlation found between the net surface charge and the variable charge ($r=0.943$, $p<0.01$) suggests that the soils are dominated by constant surface potential minerals.

Delta pH values have also been used for qualitative determination of the PZC of the soil (Keng and Uehara, 1974; Bell and Gillman, 1978; Bleeker and Sageman, 1990). PZC is the point at which the soil pH measured in 1M KCl is equal to the pH measured in water. When this unique situation occurs, the system has no net surface charge. If the pH of a soil in 1M KCl is higher than that in water, soil solution pH would lie on the acid side of the PZC, and the soil would have a net positive charge. On the other hand, if the pH of a soil in 1M KCl is lower than that measured in water, as found for the soils used in

Table 2-4. The delta pH values of the soils, the PZNC determined from ion adsorption, and the PZSE and its position in relation to ZPT obtained from titration curves in NaCl solutions.

| Soil Series | ΔpH | PZSE | PZNC | Location of PZSE with respect to ZPT cmol $kg^{-1}$ |
|---|---|---|---|---|
| Cornelia | -0.92 | 2.90 | 2.60 | 1.70, acid side |
| EauGallie | -0.87 | 3.30 | 3.43 | 0.85, acid side |
| Immokalee | -0.95 | 3.25 | 2.92 | 0.22, acid side |
| Kingsferry | -0.35 | 4.20 | 4.52 | 0.45, acid side |
| Leon | -0.57 | 3.70 | 4.00 | 0.50, acid side |
| Myakka | -0.96 | 3.20 | 3.12 | 0.65, acid side |
| Narcoose | -1.06 | 3.15 | 3.58 | 1.00, acid side |
| Oldsmar | -0.97 | 3.20 | 3.40 | 0.96, acid side |
| Ona | -1.00 | 3.20 | 3.73 | 4.70, acid side |
| Pomello | -0.78 | 3.60 | 3.90 | 0.25, acid side |
| Pomona | -0.54 | 4.10 | 4.70 | 0.50, acid side |
| Sapelo | -0.29 | 3.40 | 3.50 | 0.46, acid side |
| Smyrna | -0.28 | 4.40 | 4.90 | 0.30, acid side |
| Vero | -0.83 | ND[¶] | 3.83 | ND |
| Wabasso | -0.75 | ND | 3.43 | ND |
| Wauchula | -0.75 | 4.00 | 4.35 | 0.50, acid side |

[¶] ND is undefined.

this study, soil solution pH would lie on the alkaline side of the PZC, and the soil would carry a net negative charge. Furthermore, a large difference, in either direction, between the pH measured in water and that in 1M KCl, would indicate that the pH of the soil is several units away from the PZC. The condition above the PZC is defined by an increased net surface adsorption of $OH^-$ resulting in an increased negative surface charge and a decreased pH; thus $\Delta$pH is negative. Below the PZC, an increase in electrolyte concentration would increase the net adsorption of $H^+$ and a positive $\Delta$pH is obtained (Bell and Gillman, 1978).

Potentiometric Titrations

In the discussion that follows, PZSE and PZC will be used in the same context, to refer to the pH value at which the titration curves at different electrolyte concentrations intersect. Potentiometric titration curves for all soils are shown in Fig. 2-2. Qualitatively, the curves show electrochemical behavior that would be expected of soils or colloids that are dominated by amphoteric surfaces. From the titration curves it can be observed that there is a unique pH value (PZSE) that is independent of the indifferent electrolyte concentration and where the sign of the net surface charge undergoes reversal. As explained earlier, at a given pH on the alkaline side of the PZSE the amount of adsorbed $OH^-$ (negative charge) would increase with the electrolyte concentration, while at a given pH more acid than the PZSE, increased electrolyte concentration is associated with an increased adsorption of $H^+$ (positive charge). The PZSE values for the soils used in the study ranged from 2.90 to 4.20 (Table 2-4). These values were comparable to those obtained by Laverdiere and Weaver (1977) for spodic samples from New York and

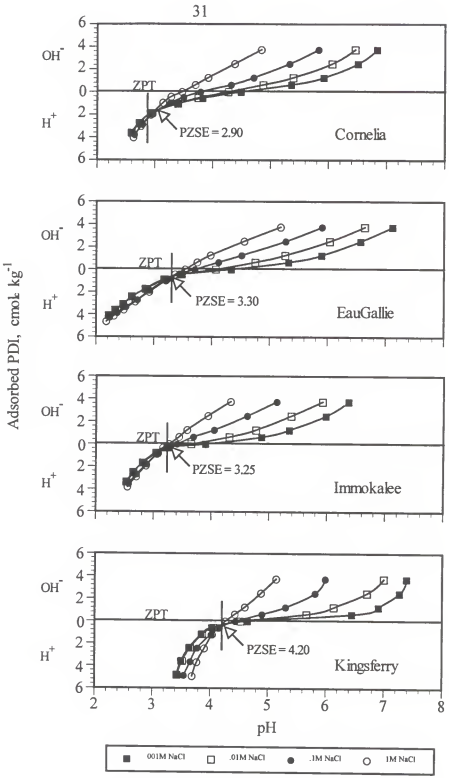



Fig. 2-2. Potentiometric titration curves for the spodic horizons. ZPT is zero point of titration; PZSE is point of zero salt effect.

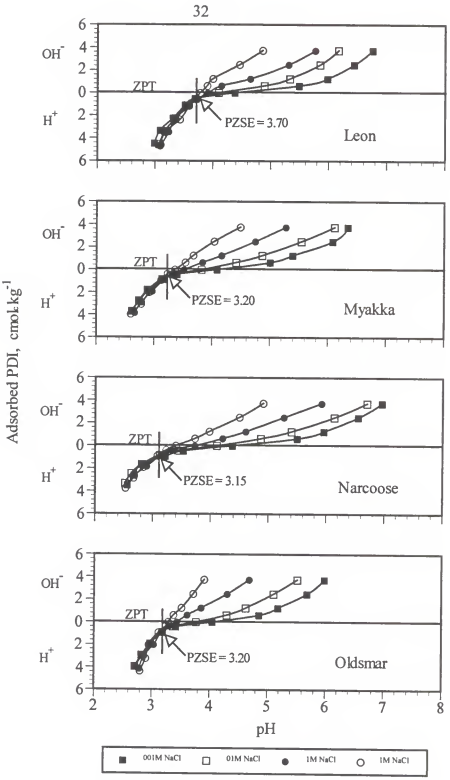



Fig. 2-2. (continued).

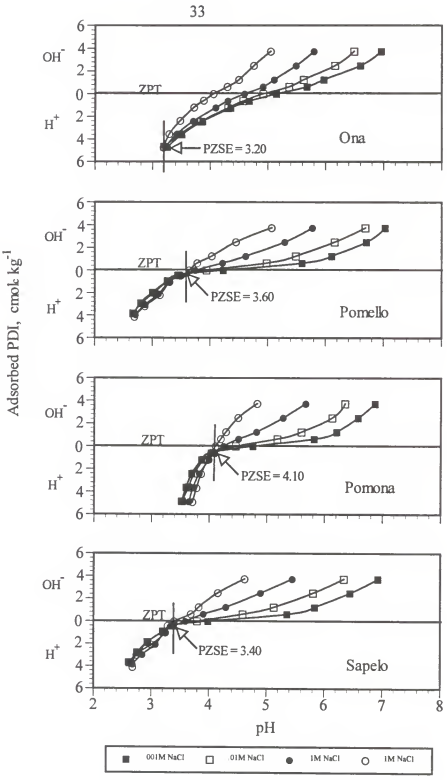



Fig. 2-2. (continued).

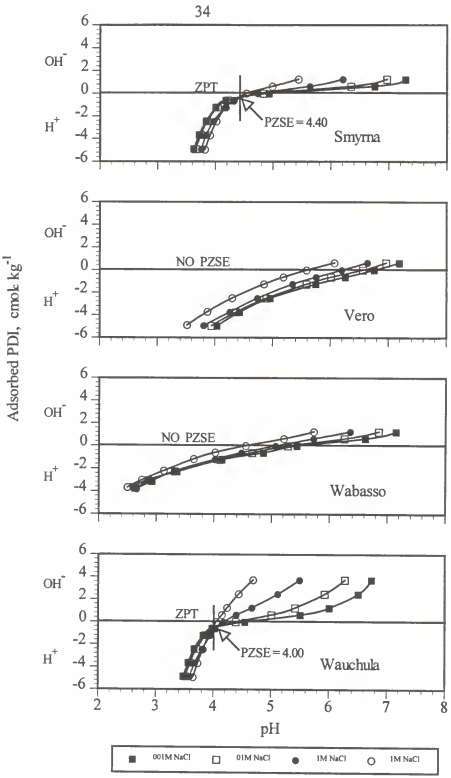



Fig. 2-2. (continued).

Canada. They were also in the same range as those reported for highly weathered soils from subtropical and tropical regions (Table 2-5). However, these values were considerably lower compared to the PZC reported for pure Al and Fe hydrous oxides (Table 2-6). The low PZSE values obtained for these soils compared to PZC values of pH 8-9 reported for pure oxides, could be due to the organic matter and the presence of permanent negative charge-containing clay minerals. Gillman (as cited by Oades et al., 1989) found a strong relationship between the point of zero charge and the organic matter content of 24 samples from six Australian Oxisols. Increasing levels of organic C resulted in a rapid lowering of the PZC from pH 6.5 to below 4.0. A similar negative correlation was reported for twelve samples from Andosols in Papua, New Guinea (Radcliffe and Gillman, 1985) and for Andosols in Costa Rica (Sollins et al., 1988). Pardo and Guadalix (1988) however, found no clear correlation between PZC and organic matter content of eight Andosol samples from Spain and Canary Islands. Such is the case with the sixteen spodic samples used in the present study. The lack of correlation can be attributed to the generally low variability in the organic matter content of the soils necessary to yield some kind of correlation, and to the presence of other soil components such as clay minerals and exchangeable Al that were masking the effect of organic matter. Oades et al. (1989) suggested two mechanisms by which organic matter could lower the PZC value of the soil. Organic matter itself has a low overall PZC (pH<2), caused by a preponderance of carboxyl groups that deprotonate at low pH values. Since the PZC value of the soil represents the mean of all the protonated and deprotonated sites on all of the variable charge components, an increase in deprotonated humic material would result

Table 2-5. Comparison of PZSE/PZC and PZNC values published in the literature for a range of soils from around the world.

| Soil/Origin | Horizon/Depth | PZSE/PZC | PZNC | Reference |
|---|---|---|---|---|
| *Brazil* | | | | |
| Dark Red Acrustox | A | 4.34 | 3.86 | Marcaño-Martinez and McBride (1989) |
| | B | 5.25 | 4.45 | |
| Red Yellow Acrustox | A | 4.25 | 3.59 | Marcaño-Martinez and McBride (1989) |
| | B | 5.18 | 5.26 | |
| Acrohumox | A | 3.60 | 2.10 | van Raij and Peech (1972) |
| | B | 4.20 | 4.40 | |
| Tropudalf | A | 3.40 | 1.90 | van Raij and Peech (1972) |
| | B | 3.80 | 2.70 | |
| *New York, USA* | | | | |
| Typic Fragiorthod | B | 4.40 | 4.40 | Laverdiere and Weaver (1977) |
| Typic Haplorthod | B | 4.50 | 4.60 | Laverdiere and Weaver (1977) |
| Aeric Haplaquod | B | 4.20 | 3.90 | Laverdiere and Weaver (1977) |
| Typic Haplorthod | E | 3.40 | 4.60 | Polubesova et al. (1995) |
| | B | 3.10 | 3.90 | |
| *Washington, USA* | | | | |
| Typic Vitrandept | 6-23 cm | 5.10 | 4.30 | Hunter and Busacca (1987) |
| | 23-42 cm | 5.10 | 4.60 | |
| Entic Cryandept | 2-16 cm | 5.20 | 4.80 | Hunter and Busacca (1987) |
| | 16-36 cm | 5.20 | 5.10 | |
| *Australia* | | | | |
| Acrohumox | A | 4.80 | 3.80 | Gillman and Bell (1976) |
| | B | 6.40 | 7.00 | |
| Haplustox | A | 4.20 | 3.00 | Gillman and Bell (1976) |
| | B | 4.40 | 3.80 | |
| *New Zealand* | | | | |
| Typic Dystrandept | A | 4.60 | 4.60 | Bolan et al. (1986) |
| Typic Fragiudalf | A | 2.80 | 1.80 | Bolan et al. (1986) |
| *Malaysia* | | | | |
| Tropeptic Haplorthod | B | 4.35 | 3.42 | Tessens and Zauyah (1982) |
| Typic Haplorthox | B | 4.30 | 4.13 | Tessens and Zauyah (1982) |
| Typic Acrorthox | B | 4.55 | 5.73 | Tessens and Zauyah (1982) |
| *Spain* | | | | |
| Typic Vitrandept | B/C | 4.50 | 3.90 | Gonzales-Batista et al. (1982) |
| Typic Dystrandept | B | 4.25 | 3.50 | Gonzales-Batista et al. (1982) |
| Typic Dystrandept | B/C | 4.75 | 4.90 | Gonzales-Batista et al. (1982) |
| Andic Haplumbrept | B | <3 | <4 | Gonzales-Batista et al. (1982) |
| *Hawaii* | | | | |
| Gibbsihumox | A | 6.30 | 6.00 | El-Swaify and Sayegh (1975) |
| Typic Hydrandept | 64-114 cm | 5.70 | 4.70 | Gonzales-Batista et al. (1982) |

Table 2-6. The point of zero charge of selected soil minerals (Adapted from Bell and Gillman, 1978).

| Mineral | Formula | PZC |
|---|---|---|
| Quartz | $SiO_2$ | 1-3 |
| Montmorillonite | $(OH)_4Si_8Al_4O_{20}$ | < 2.5 |
| Kaolinite | $(OH)_8Si_4Al_4O_{10}$ | 3 |
| Kaolinite | $(OH)_8Si_4Al_4O_{10}$ | 7.3 (edge) |
| Manganese dioxide | $MnO_2$ | 2-4.5 |
| Rutile | $TiO_2$ | 3.5-6.7 |
| Magnetite | $Fe_3O_4$ | 6.5 |
| Maghemite | $\gamma$-$Fe_2O_3$ | 6.7 |
| Goethite | $\alpha$-FeOOH | 5.9-7.2 |
| | | 7.8-8.3 |
| Hematite | $\alpha$-$Fe_2O_3$ | 8.3-9.5 |
| Amorphous iron hydroxide | $Fe(OH)_3$ | 8.5 |
| Gibbsite | $\alpha$-$Al(OH)_3$ | 7.8-9.5 |
| Boehmite | $\alpha$-AlOOH | 6.5-9.4 |
| Amorphous aluminum hydroxide | $Al(OH)_3$ | 7.5-8.0 |
| Imogolite[§] | $(OH)_3Al_2O_3SiOH$ | 6.5 |
| Allophane[§] | (Al/Si =2/1) | 6.5 |

[§] Taken from Parfitt (1980).

in a lower overall PZC value. Also, the reaction between negatively charged organic anions and positively charged oxide sites would yield more negatively charged sites resulting in the lowering of the overall PZC value.

The presence of clay minerals with a permanent negative charge would have a similar effect on the location of the PZSE. The colloidal fraction of the soils is dominated by quartz with small amounts of montmorillonite, HIV, and kaolinite (Table 2-1). As shown in Table 2-6, these minerals have PZC of 3 and lower. Addition of montmorillonite suspensions to spodic horizons prior to titrations resulted in the lowering of PZC of the soils (Laverdiere and Weaver, 1977). Furthermore, PZC was displaced away from the ZPT, on the acid side, in magnitudes equivalent to the amount of montmorillonite added. Gallez et al. (1976) attributed the low PZC values of selected soils in the tropics to the large amounts of kaolinite and quartz present in the soils in addition to the effect of organic matter.

There was no cross-over point (PZSE) for Wabasso and Vero soils. The lack of a distinct cross-over point for titration curves has been reported previously (Hendershot and Lavkulich, 1978; Cavallaro and McBride, 1984; Hunter and Busacca, 1987). This phenomenon has been attributed to a change in the surface-ordering of potential determining ions caused by increasing concentrations of NaCl. Increasing concentrations of NaCl may displace Al from the surface, altering the affinity of the surface for $H^+$ and $OH^-$.

It can be noted from the potentiometric curves that the ZPT (the equilibrium pH of the soil in a salt solution before acid or base additions) did not coincide with the PZSE.

The PZSE was displaced from 0.22 to 4.70 cmol $kg^{-1}$ on the acid side of ZPT (Fig. 2-2; Table 2-4). This phenomenon has been reported in previous studies (van Raij and Peech, 1972; Espinoza et al., 1975; Laverdiere and Weaver, 1977; Iñiguez and Val, 1982; Pardo and Guadalix, 1988) and has been attributed to the presence of permanent negative charge in the soil. The hypothesis has been that, if permanent negative charge is present, for charge reversal to occur, a certain amount of acid must be added that will yield a positive charge equivalent to that of the permanent negative charge. Consequently, the net surface charge will be zero and the pH will be independent of the electrolyte concentration. However, Uehara and Gillman (1980a) argued that since specifically adsorbed ions will influence the position of PZC, and since ZPT will depend on soil pH, the difference between PZC and ZPT does not accurately represent the amount of permanent charge in the soil. According to Sposito (1984) and Uehara and Gillman (1980b), an estimate of the permanent charge can be obtained from the difference between cation and anion adsorption at PZSE determined by titration in the absence of specific adsorption. At this pH, the variable charge ($\sigma_v$) is zero and any residual net charge must be due to the permanent component ($\sigma_p$). If cation adsorption exceeds anion adsorption, permanent charge is negative, but if there is excess anion adsorption at PZSE, permanent charge is positive. Using this approach, the permanent charge ($\sigma_p$) in the spodic horizons was estimated by substituting the PZSE value of the soil into the polynomial equations that describe the CEC and AEC curves. Permanent charge was generally small with values ranging from -0.38 to 6.66 mmol $kg^{-1}$ (Table 2-7). Based on the location of the PZSE

Table 2-7. Determination of permanent ($\sigma_p$) and variable charge ($\sigma_v$) components of the total surface charge ($\sigma_T$) of the soils. $\sigma_p$ was determined indirectly by taking the difference between AEC and CEC at PZSE. ($\sigma_v$ was obtained by subtracting $\sigma_p$ from $\sigma_T$ at natural soil pH).

| Soil | PZSE | CEC at PZSE mmol $kg^{-1}$ | AEC at PZSE mmol $kg^{-1}$ | $\sigma_p$ mmol $kg^{-1}$ | $\sigma_v$ mmol $kg^{-1}$ | $\sigma_T$ mmol $kg^{-1}$ whole soil | $\sigma_T$ mmol $kg^{-1}$ clay |
|---|---|---|---|---|---|---|---|
| Cornelia | 2.90 | 5.10 | 3.72 | -1.38 | -14.82 | -16.20 | -164 |
| Eaugallie | 3.30 | 3.83 | 4.54 | 0.70 | -12.25 | -11.55 | -246 |
| Immokalee | 3.25 | 4.81 | 2.46 | -2.35 | -11.90 | -14.25 | -594 |
| Kingsferry | 4.20 | 0.70 | 2.61 | 1.91 | -6.01 | -4.10 | -186 |
| Leon | 3.70 | 1.82 | 3.90 | -2.08 | -5.97 | -8.05 | -161 |
| Myakka | 3.20 | 4.03 | 3.66 | -0.38 | -14.67 | -15.05 | -885 |
| Narcoose | 3.15 | 1.51 | 4.93 | 3.42 | -10.04 | -6.62 | -201 |
| Oldsmar | 3.20 | 2.38 | 4.65 | 2.28 | -14.21 | -11.93 | -351 |
| Ona | 3.20 | 2.43 | 9.10 | 6.66 | -37.11 | -30.45 | -597 |
| Pomello | 3.60 | 1.49 | 3.26 | 1.77 | -7.88 | -6.11 | -170 |
| Pomona | 4.10 | 0.57 | 5.51 | 4.94 | -12.76 | -7.82 | -201 |
| Sapelo | 3.40 | 3.57 | 4.79 | 1.22 | -14.28 | -13.06 | -327 |
| Smyrna | 4.40 | 1.29 | 4.39 | 3.10 | -4.30 | -1.20 | -75 |
| Vero | ND¶ | ND | ND | ND | ND | -21.79 | -363 |
| Wabasso | ND | ND | ND | ND | ND | -13.23 | -662 |
| Wauchula | 4.05 | 1.04 | 4.95 | 3.91 | -15.07 | -11.16 | -153 |

¶ ND is undefined.

of the soils relative to ZPT, permanent charge in all soils should be negative. The presence of permanent positive charge in some soils suggests some type of isomorphous substitution in the crystallographic structure, where an element of higher valence substitutes for one of lower valence. The positive charge reported for six Oxisols from Malaysia was related to isomorphous substitution of Ti(IV) and/or Mn(IV) for Fe(III) in the Fe oxide lattice (Tessens and Zauyah, 1982). Using the ratio of Fe to Ti and/or Mn present in citrate-dithionite-bicarbonate extracts, the authors were able to calculate the positive charge of the substituted Fe oxide mineral in the Oxisols studied. Naidu et al. (1990) offered the same explanation for the occurrence of small amount of permanent positive charge in four acid Fijian soils. Although there was no research evidence of such type of substitution in the spodic horizons used in the study, the significant amount of Fe and Al oxides in these soils, as was the case for Oxisols, suggests that such a mechanism could have been a major source of permanent positive charge in these soils. Positive charge was also reported for goethite-gibbsite rich Oxisols from Brazil (van Raij and Peech, 1972; Marcaño-Martinez and McBride, 1989) and Australia (Uehara and Gillman, 1980b).

Ion Adsorption Measurements

Direct measurement of CEC and AEC by ion retention, under specified pH and electrolyte concentration presents a major advantage over potentiometric titration in that, it allows determination of both positive and negative charges as well as the net charge. Also, exchangeable Al in the soil which causes problems in the determination of the net

charge by the titration procedure can be removed by successive washings with 1M NaCl prior to the equilibration with selected NaCl concentrations.

The magnitude of positive (AEC) and negative (CEC) charges measured by $Na^+$ and $Cl^-$ retention as a function of pH in 0.01M NaCl are presented in Table 2-8. The soils carried positive and negative charges within the range of pH values studied. This finding suggests that the spodic horizons are indeed amphoteric, that is, they can have a net positive or negative charge depending on the pH of the solution. As predicted, generally for all soils, CEC increased with increasing pH, as more negatively charged sites are created through deprotonation of surface hydroxyl groups. Conversely, AEC increased with increasing acidity as more positively charged surfaces are created by protonation of OH-containing functional groups. The magnitude of negative charge varied considerably among soils. Pomona soil for example, at pH 7.33 had a CEC of 6.36 cmol $kg^{-1}$ compared to 2.74 cmol $kg^{-1}$ for EauGallie at about the same pH. This is consistent with the levels of Al and Fe in these soils. Considering oxalate-extractable Fe and Al [$(Al+Fe)_o$], Pomona had 262 mmol $kg^{-1}$ compared to 40 mmol $kg^{-1}$ for EauGallie (Table 2-2). There was very little variation in AEC of the soils. Beyond their natural pHs, positive charge in all soils was virtually zero. The net charge of the soil was estimated by subtracting cation adsorption from anion adsorption at its natural pH. Values ranged from -1.20 to -30.45 mmol $kg^{-1}$ (Table 2-7). These numbers were within the range of values reported for Oxisols from Brazil (Marcaño-Martinez and McBride, 1989) and spodic horizons from New York and Canada (Laverdiere and Weaver, 1977). Variable charge ($\sigma_v$) was obtained by subtracting permanent charge from the net charge of the soil.

Table 2-8. Distribution of positive and negative charges as determined by adsorption of $Na^+$ and $Cl^-$ in 0.01M NaCl.

| Soil | pH | $Na^+$ | $Cl^-$ | Net Charge | Specific Surface[§] | Charge Density |
|---|---|---|---|---|---|---|
| | | cmol $kg^{-1}$ | | | $m^2\ g^{-1}$ | cmol $cm^{-2} \times 10^{-7}$ |
| Cornelia | 2.49 | 0.660 | 0.665 | 0.005 | 3.83 | 0.001 |
| | 2.87 | 0.382 | 0.262 | -0.120 | | -0.031 |
| | 3.93 | 0.611 | 0.131 | -0.480 | | -0.125 |
| | 5.00 | 1.639 | 0.019 | -1.620 | | -0.423 |
| | 5.81 | 2.387 | 0.017 | -2.370 | | -0.619 |
| | 6.27 | 3.006 | 0.038 | -2.968 | | -0.775 |
| | 6.86 | 3.879 | 0.018 | -3.861 | | -1.008 |
| | 7.31 | 4.219 | 0.000 | -4.219 | | -1.102 |
| EauGallie | 2.33 | 0.243 | 0.967 | 0.724 | 16.11 | 0.045 |
| | 2.79 | 0.277 | 0.599 | 0.322 | | 0.020 |
| | 3.83 | 0.446 | 0.222 | -0.224 | | -0.014 |
| | 5.00 | 1.162 | 0.007 | -1.155 | | -0.072 |
| | 5.90 | 1.647 | 0.018 | -1.629 | | -0.101 |
| | 6.46 | 1.742 | 0.024 | -1.729 | | -0.107 |
| | 7.30 | 2.739 | 0.046 | -2.693 | | -0.167 |
| | 8.38 | 2.319 | 0.000 | -2.319 | | -0.144 |
| Immokalee | 2.47 | 0.274 | 0.512 | 0.238 | 9.89 | 0.024 |
| | 2.87 | 0.304 | 0.282 | -0.022 | | -0.002 |
| | 3.67 | 0.393 | 0.131 | -0.262 | | -0.026 |
| | 4.67 | 1.408 | 0.000 | -1.408 | | -0.142 |
| | 5.25 | 2.304 | 0.000 | -2.304 | | -0.233 |
| | 5.70 | 3.066 | 0.000 | -3.066 | | -0.310 |
| | 6.44 | 4.031 | 0.000 | -4.031 | | -0.408 |
| | 7.01 | 4.261 | 0.000 | -4.261 | | -0.431 |
| | 8.03 | 3.282 | 0.000 | -3.282 | | -0.332 |
| Kingsferry | 2.78 | 0.355 | 2.212 | 1.877 | 27.50 | 0.068 |
| | 3.27 | 0.156 | 1.234 | 1.078 | | 0.039 |
| | 3.59 | 0.143 | 0.657 | 0.514 | | 0.019 |
| | 3.94 | 0.252 | 0.152 | -0.100 | | -0.004 |
| | 5.14 | 0.394 | 0.000 | -0.394 | | -0.014 |
| | 5.71 | 0.785 | 0.000 | -0.785 | | -0.029 |
| | 6.17 | 1.204 | 0.000 | -1.204 | | -0.044 |
| | 6.71 | 3.069 | 0.000 | -3.069 | | -0.112 |
| | 6.93 | 3.716 | 0.000 | -3.716 | | -0.135 |
| | 7.34 | 6.429 | 0.000 | -6.429 | | -0.234 |

[§] Determined according to the method described by Uehara and Gillman (1981) for variable charge soils.

Table 2-8. (continued).

| Soil | pH | $Na^+$ | $Cl^-$ | Net Charge | Specific Surface[‡] | Charge Density |
|---|---|---|---|---|---|---|
| | | cmol $kg^{-1}$ | | | $m^2\ g^{-1}$ | cmol $cm^{-2} \times 10^{-7}$ |
| Leon | 2.97 | 0.158 | 0.854 | 0.696 | 59.49 | 0.012 |
| | 3.45 | 0.099 | 0.312 | 0.213 | | 0.004 |
| | 4.46 | 0.501 | 0.090 | -0.411 | | -0.007 |
| | 4.96 | 0.785 | 0.000 | -0.785 | | -0.013 |
| | 5.27 | 1.181 | 0.002 | -1.179 | | -0.020 |
| | 5.56 | 1.321 | 0.000 | -1.321 | | -0.022 |
| | 6.41 | 2.574 | 0.000 | -2.574 | | -0.043 |
| | 7.14 | 3.547 | 0.000 | -3.547 | | -0.060 |
| Myakka | 2.53 | 0.265 | 0.590 | 0.325 | 1.14 | 0.285 |
| | 2.96 | 0.217 | 0.430 | 0.213 | | 0.187 |
| | 3.83 | 0.386 | 0.177 | -0.209 | | -0.183 |
| | 4.85 | 1.482 | 0.000 | -1.482 | | -1.300 |
| | 5.31 | 2.334 | 0.000 | -2.334 | | -2.047 |
| | 5.78 | 2.904 | 0.000 | -2.904 | | -2.547 |
| | 6.48 | 3.896 | 0.000 | -3.896 | | -3.418 |
| | 7.06 | 4.368 | 0.000 | -4.368 | | -3.832 |
| | 7.68 | 4.705 | 0.000 | -4.705 | | -4.127 |
| Narcoose | 2.42 | 0.005 | 1.043 | 1.038 | 9.19 | 0.113 |
| | 2.97 | 0.095 | 0.328 | 0.233 | | 0.025 |
| | 4.02 | 0.320 | 0.085 | -0.235 | | -0.026 |
| | 4.72 | 0.641 | 0.000 | -0.641 | | -0.070 |
| | 5.28 | 1.145 | 0.000 | -1.145 | | -0.125 |
| | 5.77 | 1.295 | 0.000 | -1.295 | | -0.141 |
| | 6.84 | 2.175 | 0.000 | -2.175 | | -0.237 |
| | 7.99 | 2.365 | 0.000 | -2.365 | | -0.257 |
| Oldsmar | 2.61 | 0.027 | 0.970 | 0.943 | 17.30 | 0.054 |
| | 3.16 | 0.291 | 0.225 | -0.066 | | -0.004 |
| | 4.10 | 0.563 | 0.097 | -0.466 | | -0.027 |
| | 4.48 | 1.185 | 0.000 | -1.185 | | -0.068 |
| | 4.75 | 1.860 | 0.000 | -1.860 | | -0.108 |
| | 5.33 | 2.916 | 0.000 | -2.916 | | -0.169 |
| | 6.13 | 4.639 | 0.000 | -4.639 | | -0.268 |
| | 6.57 | 4.938 | 0.000 | -4.938 | | -0.285 |
| | 7.15 | 5.267 | 0.000 | -5.267 | | -0.304 |

[‡] Determined according to the method described by Uehara and Gillman (1981) for variable charge soils.

Table 2-8. (continued).

| Soil | pH | $Na^+$ Charge | $Cl^-$ | Net | Specific Surface[§] | Charge Density |
|---|---|---|---|---|---|---|
| | | cmol $kg^{-1}$ | | | $m^2$ $g^{-1}$ | cmol $cm^{-2}$ x $10^{-7}$ |
| Ona | 2.65 | 0.211 | 1.364 | 1.153 | 18.80 | 0.061 |
| | 2.91 | 0.216 | 1.196 | 0.980 | | 0.052 |
| | 3.47 | 0.256 | 0.530 | 0.274 | | 0.015 |
| | 4.44 | 1.016 | 0.243 | -0.773 | | -0.041 |
| | 5.13 | 1.891 | 0.145 | -1.746 | | -0.093 |
| | 5.79 | 3.034 | 0.000 | -3.034 | | -0.161 |
| | 6.06 | 3.553 | 0.000 | -3.553 | | -0.189 |
| | 6.56 | 4.367 | 0.000 | -4.367 | | -0.232 |
| | 6.97 | 5.599 | 0.000 | -5.599 | | -0.298 |
| Pomello | 2.56 | 0.138 | 0.971 | 0.833 | 27.08 | 0.031 |
| | 3.09 | 0.063 | 0.466 | 0.403 | | 0.015 |
| | 3.60 | 0.107 | 0.144 | 0.037 | | 0.001 |
| | 4.93 | 0.604 | 0.000 | -0.604 | | -0.022 |
| | 5.45 | 0.935 | 0.000 | -0.935 | | -0.034 |
| | 6.45 | 1.989 | 0.000 | -1.989 | | -0.073 |
| | 7.26 | 2.530 | 0.000 | -2.530 | | -0.093 |
| | 8.15 | 3.025 | 0.000 | -3.025 | | -0.112 |
| Pomona | 3.14 | 0.247 | 1.797 | 1.550 | 112.30 | 0.014 |
| | 3.43 | 0.138 | 1.294 | 1.156 | | 0.010 |
| | 3.67 | 0.191 | 0.606 | 0.415 | | 0.004 |
| | 4.11 | 0.253 | 0.124 | -0.129 | | -0.001 |
| | 5.18 | 0.771 | 0.000 | -0.771 | | -0.007 |
| | 5.74 | 1.450 | 0.000 | -1.450 | | -0.013 |
| | 6.13 | 2.069 | 0.000 | -2.069 | | -0.018 |
| | 6.60 | 3.628 | 0.000 | -3.628 | | -0.032 |
| | 7.01 | 4.877 | 0.000 | -4.877 | | -0.043 |
| | 7.33 | 6.361 | 0.000 | -6.361 | | -0.057 |
| Sapelo | 2.50 | 0.061 | 1.200 | 1.139 | 20.20 | 0.056 |
| | 3.00 | 0.159 | 0.420 | 0.261 | | 0.013 |
| | 3.92 | 0.475 | 0.119 | -0.356 | | -0.018 |
| | 4.99 | 1.309 | 0.003 | -1.306 | | -0.065 |
| | 5.35 | 1.696 | 0.010 | -1.686 | | -0.084 |
| | 6.14 | 2.833 | 0.005 | -2.828 | | -0.140 |
| | 6.91 | 3.420 | 0.004 | -3.416 | | -0.169 |
| | 7.62 | 4.076 | 0.000 | -4.076 | | -0.202 |

[§] Determined according to the method described by Uehara and Gillman (1981) for variable charge soils.

Table 2-8. (continued).

| Soil | pH | $Na^+$ | $Cl^-$ | Net Charge | Specific Surface[§] | Charge Density |
|---|---|---|---|---|---|---|
| | | cmol $kg^{-1}$ | | | $m^2 g^{-1}$ | cmol $cm^{-2} \times 10^{-7}$ |
| Smyrna | 3.11 | 0.252 | 1.377 | 1.125 | 40.16 | 0.028 |
| | 3.57 | 0.129 | 1.106 | 0.977 | | 0.024 |
| | 3.87 | 0.170 | 0.515 | 0.345 | | 0.009 |
| | 4.41 | 0.214 | 0.234 | 0.020 | | 0.001 |
| | 5.16 | 0.309 | 0.194 | -0.115 | | -0.003 |
| | 5.78 | 0.470 | 0.000 | -0.470 | | -0.012 |
| | 6.75 | 1.115 | 0.000 | -1.115 | | -0.028 |
| | 7.37 | 1.823 | 0.000 | -1.823 | | -0.045 |
| | 7.99 | 2.461 | 0.000 | -2.461 | | -0.061 |
| Vero | 2.49 | 0.334 | 0.912 | 0.578 | 8.46 | 0.068 |
| | 2.98 | 0.178 | 0.758 | 0.580 | | 0.069 |
| | 3.84 | 0.591 | 0.444 | -0.147 | | -0.017 |
| | 5.30 | 1.146 | 0.362 | -0.784 | | -0.093 |
| | 6.14 | 1.492 | 0.179 | -1.313 | | -0.155 |
| | 6.78 | 2.184 | 0.005 | -2.179 | | -0.258 |
| | 7.30 | 2.229 | 0.000 | -2.229 | | -0.264 |
| | 8.55 | 1.877 | 0.000 | -1.877 | | -0.222 |
| | 9.29 | 1.572 | 0.000 | -1.572 | | -0.186 |
| Wabasso | 2.45 | 0.216 | 0.444 | 0.228 | 2.24 | 0.102 |
| | 3.02 | 0.126 | 0.334 | 0.208 | | 0.093 |
| | 4.61 | 0.587 | 0.138 | -0.449 | | -0.200 |
| | 5.94 | 1.304 | 0.000 | -1.304 | | -0.582 |
| | 6.45 | 1.516 | 0.000 | -1.516 | | -0.677 |
| | 6.83 | 1.754 | 0.000 | -1.754 | | -0.783 |
| | 7.56 | 1.446 | 0.000 | -1.446 | | -0.646 |
| | 8.45 | 1.273 | 0.000 | -1.273 | | -0.568 |
| Wauchula | 2.93 | 0.182 | 1.710 | 1.528 | 82.22 | 0.019 |
| | 3.33 | 0.180 | 1.380 | 1.200 | | 0.015 |
| | 3.46 | 0.223 | 0.648 | 0.425 | | 0.005 |
| | 3.83 | 0.359 | 0.242 | -0.117 | | -0.001 |
| | 4.16 | 0.402 | 0.101 | -0.301 | | -0.004 |
| | 5.18 | 1.073 | 0.000 | -1.073 | | -0.013 |
| | 6.07 | 2.426 | 0.000 | -2.426 | | -0.030 |
| | 6.91 | 4.968 | 0.000 | -4.968 | | -0.060 |
| | 7.22 | 6.054 | 0.000 | -6.054 | | -0.074 |

[§] Determined according to the method described by Uehara and Gillman (1981) for variable charge soils.

These values ranged from -4.3 to -37.1 mmol $kg^{-1}$. Soils with variable charge higher than their net charge possess a permanent positive charge.

The plot of CEC and AEC versus pH for all soils are shown in Fig. 2-3. The point at which AEC equals CEC is the PZNC. In the graph, it is the pH value at which the AEC-CEC curve intersects the x-axis at y=0. The PZNC values obtained for the soils ranged from 2.60 to 4.90. Although these values showed positive correlation with PZSE ($r=0.941$, $p<0.01$) in all but three soils, PZSE was higher than PZNC. It was interesting to note that in the soils where PZNC was higher, permanent positive charge was present. PZNC was displaced from PZSE by a magnitude proportional to the amount of permanent positive charge in the soil. Theoretically, PZSE values generated from titration curves should be higher than PZNC obtained from ion retention. This is because with ion adsorption, there is a more complete release of permanent negative charge in the absence of exchangeable Al which should have been removed by the successive washings prior to equilibration. In the case of potentiometric titration, with soils containing permanent negative charge, it is likely that a considerable proportion of the negative charge is balanced by strongly adsorbed $Al^{3+}$ giving rise to higher values for PZSE. Laverdiere and Weaver (1977) reported good agreement between the two values for a Haplorthod but Marcaño-Martinez and McBride (1989) contend this is not always the case. Since ion adsorption technique measures both permanent and variable charge, while titration method is thought to measure only variable charge, agreement between the two methods would require very low permanent charge. Using this argument, it seems logical that for soils containing permanent negative charge, PZSE will always be higher than PZNC. In

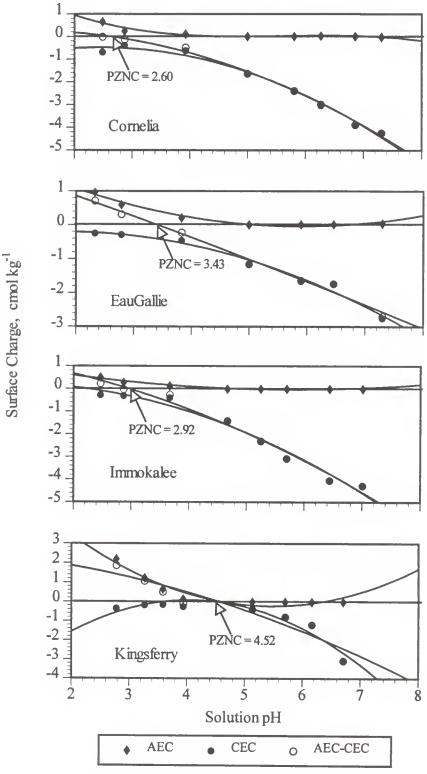



Fig. 2-3. Dependence on solution pH of CEC and AEC of the spodic horizons measured by the adsorption of Na and Cl ions. PZNC is point of zero net charge.

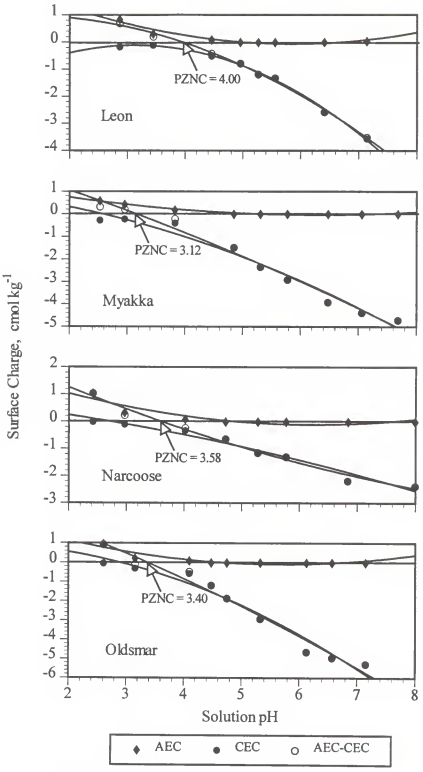



Fig. 2-3. (continued).

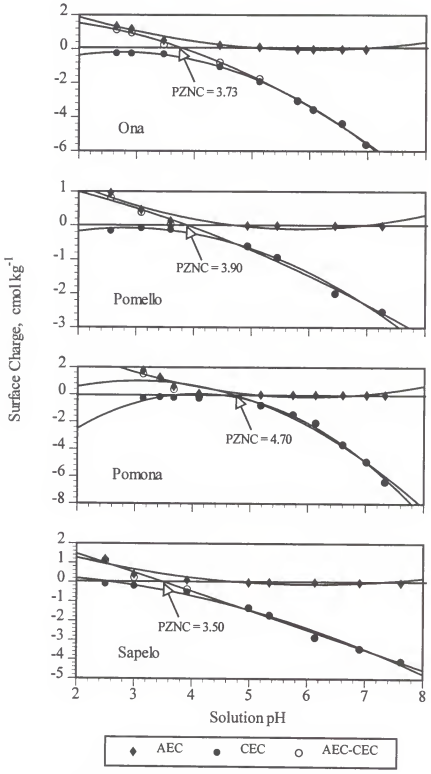



Fig. 2-3. (continued).

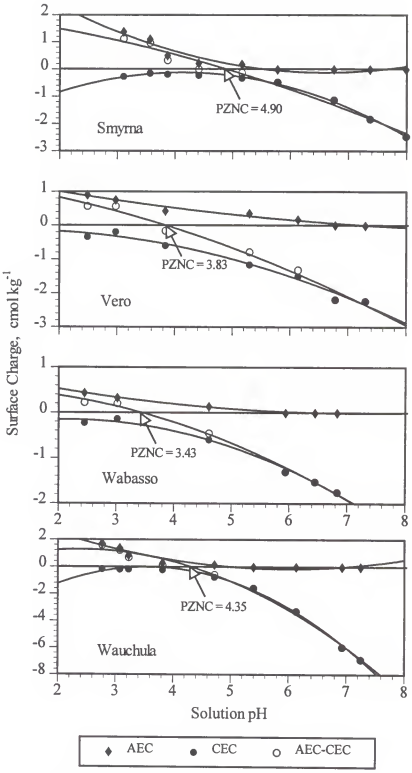



Fig. 2-3. (continued).

soils containing permanent positive charge, as was the case for many of the soils in the study, PZSE is expected to be lower than PZNC. Results reported for Oxisols from Australia (Uehara and Gillman, 1980b) and from Brazil (Marcaño-Martinez and McBride, 1989) validate the findings of the present study. Additionally, PZSE will not coincide with the PZNC in cases where protons and hydroxyls used in the potentiometric titration are consumed in reactions other than charge balancing (Parker et al., 1979) and where there is specific adsorption of index ions during charge measurements by the ion retention method (Sposito, 1981).

Application of Models to Experimental Data

The experimental data obtained from ion adsorption as a function of pH at 0.01M NaCl were compared with curves predicted by the Gouy-Chapman and Stern theories. The net negative surface charge densities of the soils at their natural pH were calculated and plotted as a function of surface potential (Fig. 2-4). The values for surface potential were calculated from Eqn. 2-5 using the PZNC values determined from the ion adsorption measurements. Along with the experimental data in Fig. 2-4 were the theoretical curves for Gouy-Chapman and Stern relationships for reversible interfaces in the presence of symmetrical 1:1 electrolyte. The Gouy-Chapman curve was constructed by initially assigning values to $\psi_o$ and then substituting these values into Eqn. 2-1 to obtain surface charge density, $\sigma_o$. Construction of the Stern curve involved the use of Eqns. 2-6, 2-7, 2-8, and 2-9. The value taken for $N_i$ was $10^{15}$ $cm^{-2}$ and for $(\epsilon'/4\pi d)$ was 100$\mu$F $cm^{-2}$. Specific adsorption of ions was assumed to be negligible, thus $\phi$=0. Initially, arbitrary values were assigned to $\psi_d$ and substituted into Eqn. 2-7 and 2-8 to obtain $\sigma_1$ and $\sigma_2$,

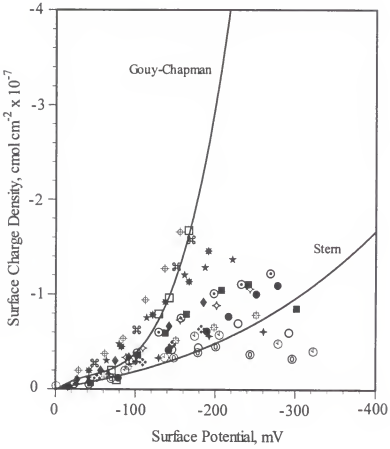



Fig. 2-4. Experimental plot of net surface charge density versus surface potential relative to the theoretical curves predicted by the Gouy-Chapman and Stern models for reversible interfaces. Data used were obtained from ion adsorption at 0.01M NaCl.

respectively. These values were then substituted into Eqn. 2-6 to obtain $\sigma_o$, the sum of the charge in the Stern layer ($\sigma_1$) and the charge in the diffuse layer ($\sigma_2$). Values for $\psi_o$ were found using Eqn. 2-9.

There was a relatively good agreement between observed values and those predicted by the Gouy-Chapman theory. Although in some cases, the soils were characterized by having a surface charge density that was greatly in excess of that predicted by the model. The experimental values obtained by van Raij and Peech (1972) for Brazilian Oxisols were lower than those predicted by the model, although agreement tended to improve with decreasing electrolyte concentration and with decreasing surface potential. Similarly, Iñiguez and Val (1982) reported adequate prediction of their experimental data by Gouy-Chapman model only when the electrolyte concentration was 0.01M NaCl, the same concentration used in the present study.

The Stern model seemed to describe the values better at higher surface potential. This is consistent with the criticism of the Gouy-Chapman model, that at moderately high surface potentials ($\psi_o \geq$ 100 mV), unrealistically high values are predicted for the amount of counterions adsorbed into the diffuse double layer. van Raij and Peech (1972) and Iñiguez and Val (1982) obtained better fit of their experimental data with Stern theory than with Gouy-Chapman. Laverdiere and Weaver (1977) working with spodic horizons from selected Spodosols in New York and Canada obtained satisfactory results for only two soils. Both models somewhat overestimated the values for the other soils and questioned the applicability of such models for soil systems as complex and as heterogeneous as the spodic horizons. They claimed that the observed charge properties

of the spodic horizons which were strikingly similar to constant surface potential colloids at least qualitatively, were a composite effect of the various constituents rather than proton adsorption-desorption at a relatively homogeneous surface or interface.

Correlation of Surface Charge Parameters with Soil Properties

The effects of different soil constituents on the surface charge properties of the soils are examined using simple correlation analysis. Only variables which show some type of correlation with at least one of the charge properties are included in Table 2-9. Relationships among charge properties are shown in Fig. 2-5.

Delta pH values correlated significantly with the net surface charge of the soils but not with either the permanent or variable charge component (Fig. 2-5). As pointed out earlier, while a large negative ΔpH value indicates a high negative surface charge density, nothing can be said about whether the charge is variable or permanent (Uehara and Gillman, 1981). However, a positive correlation was found between the net surface charge and the variable charge in the soils, indicating that the constant surface potential minerals were the main source of charge in the spodic horizons studied. Large negative ΔpH values were associated with high levels of organically bound Al ($Al_p$) (Table 2-9). Uehara and Gillman (1981) attributed high levels of exchangeable Al to the abundance of permanent charge ($\sigma_p$) in the soils.

There was a good agreement between PZNC and PZSE values obtained in the present study and those published in the literature for different soils (Fig. 2-6), although in most cases, PZNC was lower than PZSE. As explained earlier, PZNC and PZSE would be equal only in a pure variable charge system. It was not surprising that both

Table 2-9. Correlation of surface charge parameters with chemical soil properties. Only soil variables showing significance with at least one of the surface charge properties are included.

| Soil Variable | ΔpH (n=16) | PZSE (n=14) | PZNC (n=14) | $\sigma_p$ (n=16) | $\sigma_v$ (n=16) | $\sigma_T$ (n-16) |
|---|---|---|---|---|---|---|
| $Al_p$ | 0.515* | 0.747** | 0.724** | 0.635* | 0.027 | 0.288 |
| $Al_o$ | 0.494 | 0.725** | 0.709** | 0.652* | -0.004 | 0.264 |
| $Al_d$ | 0.367 | 0.625* | 0.679** | 0.784* | -0.236 | 0.073 |
| $Al_T$ | 0.505 | 0.697** | 0.691** | 0.642* | 0.003 | 0.252 |
| Σ Bases | -0.222 | -0.376 | -0.056 | 0.407 | -0.875** | -0.619* |
| ECEC | -0.244 | -0.509 | -0.135 | 0.089 | -0.875** | -0.671** |

*,** Significant at $p<0.05$ and $p<0.01$, respectively.

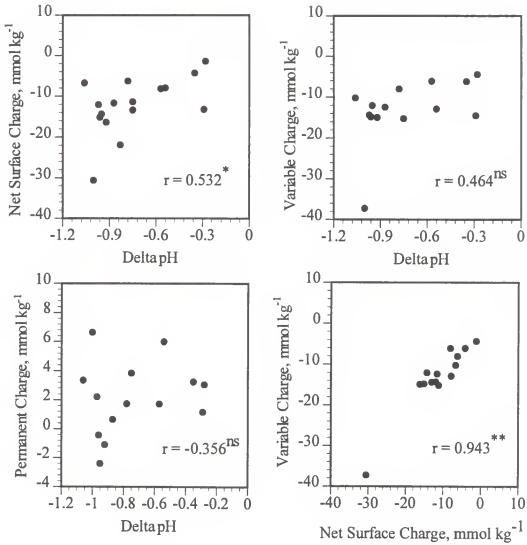



Fig. 2-5. Correlation among delta pH, permanent, variable, and total net surface charge of the soils. *, ** Denote significance at $p<0.05$ and $p<0.01$, respectively.

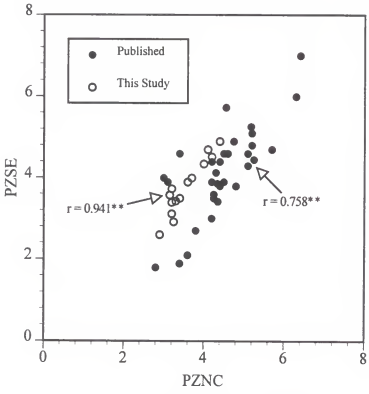



Fig. 2-6. Comparison of PZNC and PZSE values obtained for soils used in this study and those published in the literature.

parameters gave positive correlation with all forms of Al in the soil. Recall that these spodic horizons are dominated by Al. And from Table 2-9, it can be seen that these minerals in pure form have a PZC of 7.5-8.5. Therefore, their presence in the soil would shift both PZSE and PZNC to higher values. Pardo and Guadalix (1988) reported a significant correlation between $Al_2O_3$ content and PZC of the soils ($r=0.801$, $p<0.01$). Similar results were obtained by Radcliffe and Gillman (1984) who obtained a high correlation not only with the $Al_2O_3$ but also with the $Fe_2O_3$ content of the soils. The lack of correlation between the forms of Fe in the soil and the PZNC and PZSE values was attributed to generally low levels of Fe in the soils. If present in high amounts, Fe minerals should shift the PZNC and PZSE to higher values because of their high PZC values in pure form.

No quantitative mineralogical data could be correlated with the charge properties. However, based on the types of minerals present in the soils, quartz with a PZC of less than 3, more than any silicate minerals would have caused significant reduction in the PZSE and PZNC of the soils. The effect of organic matter on lowering the PZC of the soils has been reported by many researchers. Although, a rather weak correlation was found between organic matter and the PZSE and PZNC values, the net effect of organic matter was to lower PZSE and PZNC values.

There was a significant negative correlation between the net surface charge and the concentrations of exchangeable bases in the soils (Table 2-9). Correlation was even better when there is high concentration of Al in the exchange sites (ECEC). Specific adsorption of divalent cations like Ca and Mg renders the surface more positive resulting

in a surface with low negative charge. The effect is greater with Al due to its high valence and shape that provide effective blocking of negatively charged sites.

The preceding discussion was based solely on correlation (or lack of it) between any two variables. As mentioned earlier, the presence of Fe and Al oxides would increase the PZC towards higher values, while the presence of minerals with structurally negative charge as well as organic matter would tend to reduce this value. However, it must be taken into account that when these constituents are altogether present in the soil, which is what normally happens, interactions occur among these components which modify their individual net charge. Thus, the sign and magnitude of the net surface charge of a soil under specific conditions are a composite effect of the different constituents interacting with one another and not by just one single component.

Effect of P Loading on Charge Properties

It has been suggested that adsorption of phosphate onto surfaces of metallic oxides and hydroxides shifts the PZC of the soil to a lower pH value. The hypothesis has been that the additional negative charges created by specific adsorption of phosphate would require more cations to balance these charges and an increase in the CEC should be noted.

Results of potentiometric titration for P-treated EauGallie and Wauchula soils are shown in Fig. 2-7 and Fig. 2-8, respectively. As expected, a progressive lowering of the PZSE was observed for both soils with each level of P added. PZSE values ranged from 3.30 to 2.60 for EauGallie, and from 4.05 to 3.08 for Wauchula. These values correspond to a linear drop of 0.028, and 0.016 PZSE units per millimole of P added.

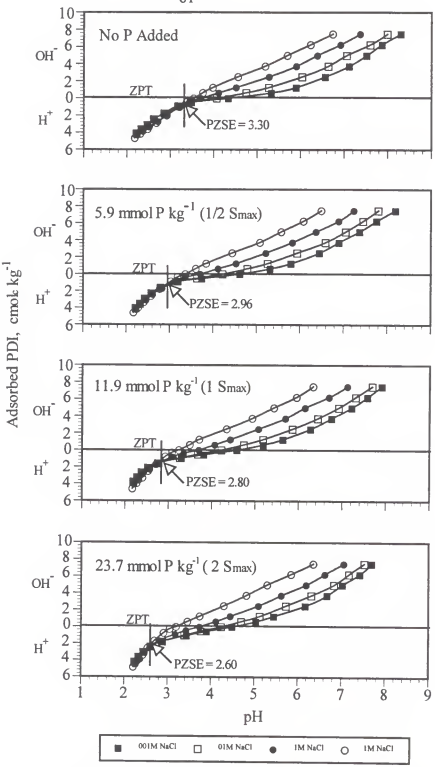



Fig. 2-7. Shifts in PZSE for EauGallie soil as influenced by P loading. ZPT is zero point of titration; PZSE is point of zero salt effect.

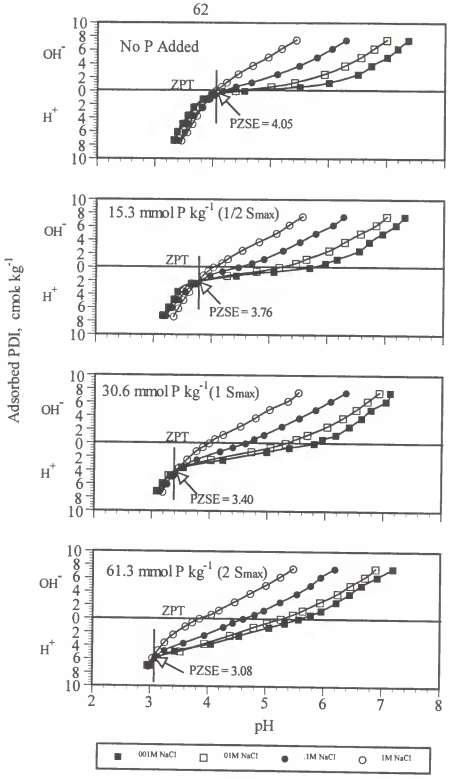



Fig. 2-8. Shifts in PZSE for Wauchula soil as influenced by P loading. ZPT is zero point of titration; PZSE is point of zero salt effect.

The lowering of PZC values following P addition has been reported by several researchers ( Sawhney, 1974; Wann and Uehara,1978; Laverdiere, 1982; Barrow and Ellis, 1986; Bolan, 1986).

There appears to be a limit to the amount of P that can be added to the soils beyond which the potentiometric curves will not intersect. As the net charge on the soil becomes increasingly negative with each increment of P added, PZSE is displaced farther and farther away from the ZPT until the crossover point starts to disappear (Fig. 2-7; 2-8). The increase in negative charges estimated from the distance between the PZSE and the ZPT ranged from 0.85 to 2.40 cmol $kg^{-1}$ for EauGallie, and from 0.50 to 5.80 cmol $kg^{-1}$ for Wauchula. The increase in negative charge following P adsorption implies that phosphate was specifically adsorbed by Fe and Al oxides in the soils. Depending on solution pH, these oxides carry a net positive, net zero or net negative charge. Specific adsorption of phosphate can occur by ligand exchange with aquo (M-$H_2O$), hydroxo (M-OH) or ol (M-OH-M) groups. At acid pH values, such as those found in the soils used in the study, the reactivity of these groups to ligand exchange is in the order aquo≥ hydroxo > ol (Graham and Thomas, 1947). Rajan et al. (1974) in their study using hydrous aluminum oxide, showed that at low P concentration, phosphate was adsorbed on positive sites displacing water that was coordinated to the oxide surface.

$$Al\text{-}H_2O]^{1+} + H_2PO_4^- \rightleftarrows Al\text{-}H_2PO_4]^0 + H_2O$$

The exchange of phosphate with aquo groups would add negative charge to the surface but would not increase the concentration of the hydroxyl ions in solution. With increase in P concentration, P was adsorbed mainly by displacing hydroxo groups.

$$Al\text{-}OH]^0 + H_2PO_4^- \rightleftarrows Al\text{-}H_2PO_4]^0 + OH^-$$

This reaction would not affect surface charge but would release equivalent amounts of hydroxyl ions into solution. From the data in Table 2-10, it can be seen that addition of P increased both the pH and CEC of the soils. For EauGallie, the pH at ZPT increased from 4.07 (at 0 P addition) to 4.22 (at ½ $S_{max}$) and was rather constant at higher P concentrations. The same trend was observed for the CEC of the soil. However, in Wauchula, both pH and CEC increased with each increment of added P. Solution pH increased from 4.39 (at 0 P addition) to 5.36 (at 2 $S_{max}$). Likewise, CEC increased from 10.73 to 34.49 mmol $kg^{-1}$. The magnitude of increase in pH and CEC decreased with increasing levels of added P. According to Rajan et al. (1974) the aquo and hydroxo groups have similar reactivities, thus it is likely that at ½ $S_{max}$ where the largest increase in pH and CEC were noted, both types of replacement were simultaneously occurring in the soils. At higher P concentrations, where P adsorption via these mechanisms was nearly complete, the hydroxyl bridges linking Al atoms would break into smaller units creating new adsorption sites. This mechanism might have been responsible for small increases in the CEC of Wauchula soil at P levels beyond its sorption maximum capacity. The differences in the effect of P addition on pH and CEC can be attributed to the levels of Fe and Al in the soils. Although both soils were dominated by Al, Wauchula had far more Al than Fe compared to EauGallie (Table 2-2). The mole ratio of total Al to Fe was 45:1 for Wauchula and 2:1 for EauGallie. These numbers suggest that in Wauchula, ligand exchange of P with aquo and hydroxo groups coordinated at the Al oxide surface

Table 2-10. Influence of P additions on the surface charge characteristics of EauGallie and Wauchula soils.

| Soil | P Added, mmol P $kg^{-1}$ | PZSE | $pH_{ZPT}$ | Location of PZSE with respect to ZPT cmol P $kg^{-1}$ | CEC[§] mmol $kg^{-1}$ | AEC[§] mmol $kg^{-1}$ | Net Charge[§] mmol $kg^{-1}$ |
|---|---|---|---|---|---|---|---|
| EauGallie | 0.0 (No P) | 3.30 | 4.07 | 0.85, acid side | 11.62 | 0.07 | -11.55 |
| | 5.9 (1/2 $S_{max}$) | 2.96 | 4.22 | 1.40, acid side | 13.46 | 0.00 | -13.46 |
| | 11.9 (1 $S_{max}$) | 2.80 | 4.22 | 1.50, acid side | 12.21 | 0.00 | -12.21 |
| | 23.7 (2 $S_{max}$) | 2.60 | 4.24 | 2.40, acid side | 12.32 | 0.00 | -12.32 |
| Wauchula | 0.0 (No P) | 4.05 | 4.39 | 0.50, acid side | 10.73 | 0.00 | -10.73 |
| | 15.3 (1/2 $S_{max}$) | 3.76 | 5.17 | 2.16, acid side | 15.54 | 0.00 | -15.54 |
| | 30.6 (1 $S_{max}$) | 3.40 | 5.31 | 4.40, acid side | 23.96 | 0.00 | -23.96 |
| | 61.3 (2 $S_{max}$) | 3.08 | 5.36 | 5.80, acid side | 34.49 | 0.00 | -34.49 |

[§] Data obtained from ion adsorption at the natural soil pH.

was the major source of negative charge. For EauGallie, adsorption of P onto Al and Fe were equally important sources of CEC.

## Summary and Conclusions

Results from potentiometric titration and ion adsorption show that the colloidal fraction of spodic horizons from selected Florida Spodosols was dominated by colloids whose charge depended on pH and electrolyte concentration of the soil solution. The pH values at which the net surface charge underwent reversal (PZSE) ranged from 2.90 to 4.20. Although Al oxides along with organic matter apparently dominated the charge properties, PZSE did not coincide with ZPT. In all soils, PZSE was displaced from 0.22 to 4.70 cmol $kg^{-1}$ on the acid side of ZPT indicating presence of clay minerals with a permanent negative charge. The soils carried positive and negative charges within the range of pH values studied. The pH values at which there was equal adsorption of cations and anions by the soil (PZNC) ranged from 2.60 to 4.90. These numbers agreed fairly well with those obtained from potentiometric titrations. The electrochemical behavior of the soils was adequately predicted by the theoretical models of Gouy-Chapman and Stern for reversible interfaces.

The soils have relatively low CEC values at their natural pH. Treatment of soils with phosphate displaced the PZSE to lower pH values thereby increasing CEC and the net negative charge of the soil. This is beneficial from the standpoint of plant nutrition. High CEC values would ensure an adequate supply of basic cations for the nutritional needs of the plants. However, considering the location of the spodic horizon in the

profile, which in most cases is below the plow layer, results of this study might be of little practical importance in terms of managing these soils for agronomic purposes.

Results of the present study should have greater significance in terms of understanding the role of the spodic horizon in regulating P inputs to lakes and streams. For spodic horizons whose colloidal fraction is dominated by variable charge materials, the overall effect of P addition can be summarized by the following equation

$$\sigma_v = \text{constant } (pH_{pzc}\text{-}pH)$$

Phosphorus loading would increase CEC by displacing the PZC to a lower value, thus making ($pH_{PZC}$-pH) and the surface charge more negative. However, there was a limit to the amount of P that can be added to the soil beyond which, further increase in negative surface charge would be minimal, and this was found to be directly related to the number of sorption sites in the soil. The system will continue to adsorb P until reaction of P with the Al and Fe oxide surfaces is "complete". Thus, application of P to these soils in excess of their maximum sorption capacity would result in unacceptable amounts of P in the drainage water.

# CHAPTER 3
# SORPTION AND RELEASE OF PHOSPHORUS BY THE SPODIC HORIZON UNDER AEROBIC AND ANAEROBIC CONDITIONS

## Introduction

The use of agricultural land for disposal of industrial, municipal, and animal wastes has been a well-established practice for many years (Sommers and Sutton, 1980). When considering the soil as a medium for wastewater renovation, it is essential to know its nutrient-assimilative capacity, in order to predict the amount of nutrients that can be applied to the soil without risk to the environment. Excessive application of various wastes to soils could lead to accumulation and eventual transport of nutrients such as P, and other contaminants to adjacent water bodies. Lake Okeechobee, for example, the major aquatic resource for water storage, wildlife, and recreation in south Florida is becoming increasingly eutrophic due to excessive P loading from the dairy farms in the adjacent watersheds (Bottcher et al., 1995). Transport of P from dairy farms to receiving waters in the basin is exacerbated by adverse soil and hydrologic conditions (Allen, 1987). Efficient retention of P by soil is dependent, among other factors, on soil pH and the amount and nature of sorbing components in the soil (Syers and Iskandar, 1981). Most of the dairy sites in the Lake Okeechobee Basin are located on Spodosols on a relatively level landscape. These soils consist of three primary horizons, namely, A, E, and Bh. The A horizon is sandy with small amounts of organic matter and generally has a

depth of 15 to 20 cm. The E horizon located immediately below the A horizon is highly eluted with thickness ranging from 20 to 140 cm depending on the soil type. Below the E horizon is the spodic (Bh) horizon in which Fe and Al oxides along with organic matter have accumulated. This characteristic composition coupled with low pH contribute to the high P sorption capacity of the Bh horizon. Phosphorus moving from the surface horizon is generally thought to accumulate in the Bh horizon. However, during the summer rainy periods, limited permeability in the Bh horizon would give rise to shallow water tables which would not only restrict movement of P into the Bh horizon, but also, depending on the period of submergence, may trigger changes in pH and redox potential of the soil. These electrochemical changes could influence the dynamics of P in the Bh horizon and consequently, its transport to watercourses.

The physico-chemical changes following flooding influence both the forms of solid phase P and the nature of P-sorbing surfaces and consequently, the distribution of labile P between solid and solution (Tian-ren et al., 1989). Reduction of soil by flooding and re-oxidation upon drainage have been shown to cause marked variations in P sorption characteristics of the soils (Khalid and Patrick, 1977; Willett and Higgins, 1978; Holford and Patrick, 1981; Willett and Cunningham, 1983; Bradley et al., 1984; Sah and Mikkelsen, 1986, 1989). Most of the changes in reactivity of P in such soils have been ascribed to changes in Fe chemistry, as Al is stable under changing redox conditions. Aluminum can significantly influence the dynamics of P with changes in pH, ionic strength of solution, and solution P concentration (Tian-ren et al., 1989).

Transport of P with water in soils is largely dependent upon the rate and extent of P retention by soil components. The high P sorption capacity of acid soils has often been associated with Fe and Al oxide surfaces (Juo, 1981; van der Zee and van Riemsdijk, 1986; Loganathan et al., 1987; Parfitt, 1989; Wada et al., 1989; Borggaard et al., 1990). Significant correlations were found between P sorption and oxalate-extractable Al and Fe in Spodosols from British Columbia (Yuan and Lavkulich, 1994). Similarly, van der Zee and van Riemsdijk (1986, 1988) reported that P sorption in different acid soils from the Netherlands was linearly related to the sum of oxalate-extractable Fe and Al. In a range of Danish soils, P sorption was a function of citrate-dithionite-bicarbonate (CDB)-extractable Fe and oxalate-extractable Fe and Al (Borggaard et al., 1990). CDB-extractable Fe and Al, oxalate-extractable Al and clay content were major contributors to P sorption in Australian soils (Singh and Gilkes, 1991). Several researchers have reported positive relationships between the organic matter content of soils and P sorption (Lopez-Hernandez and Burnham, 1974; Mizota et al., 1982; Owusu-Bennoah and Acquaye, 1989; Sanyal et al., 1990). The role of organic matter in increasing the ability of soils to sorb P has often been attributed to its association with cations such as Fe, Al, and Ca.

Quantitative descriptions of short-term reactions between soil components and P have often been made with the Langmuir, Freundlich, and Temkin equations. Though these equations were originally derived to describe the adsorption of gases by solids, in many cases these models were able to provide adequate mathematical descriptions of P sorption in soils. By far, the most widely used model is the Langmuir equation which

was first applied to P sorption on soils by Olsen and Watanabe (1957). Assumptions inherent in the Langmuir equation include a constant heat of adsorption with surface coverage, implying uniform adsorption sites with no interaction between adsorbed species, and that monolayer adsorption is the maximum possible. It has a distinct advantage over Freundlich and Temkin equations in that, it allows estimation of sorption maximum and a constant that is related to the P bonding energy. The Freundlich equation which was originally empirical, implies that the energy of adsorption decreases logarithmically with increasing saturation of the surface. Although it does not provide any measure of an adsorption maximum, the Freundlich coefficient K can be regarded as a hypothetical index of P sorbed from a solution having unit equilibrium concentration (Sanyal and De Datta, 1991). The Temkin equation was proposed by Bache and Williams (1971) for describing P sorption by soils. The model which was essentially derived from Langmuir equation, assumes that the energy of adsorption decreases linearly with increasing surface coverage. The phosphorus sorption isotherms plotted according to the Temkin equation were reported to deviate from linearity in a manner similar to that from Langmuir plots. Other adsorption models used to quantitatively describe P sorption in soils include, the Langmuir multi-surface equation (Holford et al., 1974), the mechanistic model of Bowden et al. (1973), the quadratic equation (Yuan and Lucas, 1982; SAS, 1985), and a least squares fit of the several empirical modifications of the Langmuir equations (Gunary, 1970).

The conformance of experimental sorption data to an adsorption isotherm equation does not provide specific information about the actual mechanism of a sorption

process in soils. Indeed, Veith and Sposito (1977) and Sposito (1982) demonstrated that under the conditions of their study, the Langmuir equation cannot be used statistically to determine whether sorption or precipitation is occurring during the removal of anions such as phosphate from the soil solution. The constant parameters obtained from adsorption equations cannot be interpreted in terms of surface reactions, unless independent evidence is provided to explain their chemical meaning (Sposito, 1982).

Despite the limitations imposed by the assumptions surrounding the different adsorption models, the P sorption parameters obtained from these equations can provide useful descriptions of P sorption in soils. The spodic horizons, as described earlier, are characterized by low pH and a significant amount of noncrystalline Fe and Al in their colloidal fraction, thus it was hypothesized that the spodic horizons would exhibit high sorption capacity, and therefore would act as sinks for P.

This study was conducted to (i) compare the P sorption and release properties of spodic horizons from selected Florida Spodosols under aerobic and anaerobic conditions, (ii) to evaluate the relationships among P sorption parameters and selected soil properties, and (iii) to identify the soil variables that best predict P sorption.

## Materials and Methods

### Selection and Description of Soils

Samples from spodic horizons representing sixteen Spodosols from fourteen Florida counties were used in the study (Fig. 3-1). Thirteen of the sixteen soil samples belong to the great group Alaquods; the rest are Haplorthods. Alaquods are

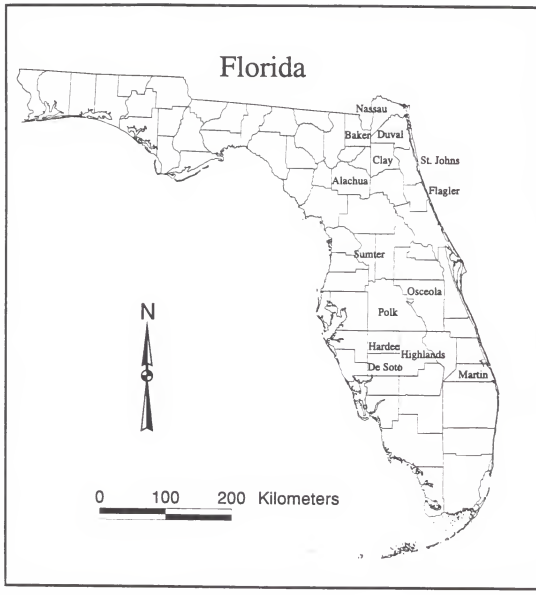



Fig. 3-1. Location of the spodic samples used in this study.

characterized by a fluctuating water table and a spodic horizon that is principally an accumulation of Al and organic matter. Haplorthods are the more or less freely drained Spodosols in which Fe, organic matter, and Al have accumulated (Soil Survey Staff, 1996). The soils which cover a wide range of Fe and Al levels commonly found in Florida Spodosols were chosen from a host of samples that had been archived up to 15 years (Harris et al., 1995). The selection process was aided by an electronic database called RAMIS which is a compilation of the characterization data for Florida soils. The program was developed jointly by the University of Florida Soil and Water Science Department and the USDA Soil Conservation Service as part of the Florida Cooperative Soil Survey program. Once the final selection was made, aliquots of stored samples were obtained from the archive and used for this study. Harris et al. (1995) assumed that the chemical reactivity toward P of the archived samples would be similar to the same soils under field conditions.

Initial Soil Characterization

Routine analyses. Soil reaction (pH) was measured in water and 1M KCl using a 1:1 soil:solution ratio (McLean, 1982). Organic carbon was estimated by rapid oxidation with a hot mixture of $K_2Cr_2O_7$ and $H_2SO_4$ (Nelson and Sommers, 1982). Exchangeable Ca, Mg, K, and Na were extracted from a 0.1M $BaCl_2$ solution following a 2-hour equilibration (Gillman, 1979). Exchangeable Al was determined by extraction with 1M KCl (Barnhisel and Bertsch, 1982). The sum of exchangeable cations and Al was taken to represent the effective cation exchange capacity of the soil (ECEC) (Juo et al., 1976). Net surface charge was estimated by taking the difference between anion exchange

capacity (AEC) and cation exchange capacity (CEC) of the soils obtained from direct adsorption of $Na^+$ and $Cl^-$ (Schofield, 1949).

The elemental concentrations of Al, Fe, and P were determined by digesting finely ground sample in nitric-perchloric acid mixture (Olsen and Sommers, 1982). Similarly, the analysis of Al, Fe, and P in the digestate was done by ICAP emission spectrophotometry.

Fe and Al forms. The various pools of Fe and Al in the soils were determined by selective dissolution. Reactive Al was estimated by extraction with 1M $CuCl_2 \cdot H_2O$ (Juo and Kamprath, 1979). Aluminum and Fe associated with organic matter were extracted with 0.01M $Na_4P_2O_7$ (Wada and Higashi, 1976). Amorphous and crystalline forms of Al and Fe were dissolved in acidified 0.2M $(NH_4)_2C_2O_4$ (McKeague and Day, 1966), and citrate-dithionite-bicarbonate (Mehra and Jackson, 1960), respectively. Iron and Al in the extracts were analyzed using an Inductively Coupled Argon Plasma emission spectrophotometer.

Phosphorus fractionation. Phosphorus originally present in the spodic horizons was separated sequentially into loosely bound P, Fe/Al-P, and Ca-P by extraction with 1M $NH_4Cl$, 0.1M NaOH, and 0.5M HCl (Hieltjes and Lijklema, 1980) (Fig. 3-2). Moderately labile organic P was estimated by taking the difference between P in digested and undigested NaOH extract. Digestion was done in persulfate-sulfuric acid mixture at 380°C (APHA, 1985). All P determinations were done using the procedure of Murphy and Riley (1962) on a Technicon Auto Analyzer II. The highly resistant P fraction in the residue left after HCl extraction, was estimated by subtracting the amount of all P

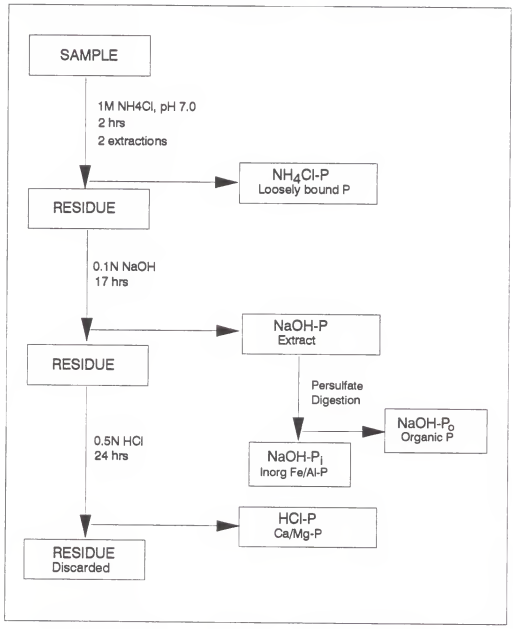



Fig. 3-2. Phosphorus fractionation scheme used in this study (Modified from Hieltjes and Lijklema, 1980).

fractions combined from the total P obtained by perchloric digestion. An estimate of native sorbed P in soils was obtained by the anion-exchange resin- impregnated membrane (AEM) methodology developed by Cooperband and Logan (1994).

Phosphorus Sorption Studies

Aerobic. Duplicate 1-gram samples were placed in 50-mL centrifuge tubes. The samples were suspended in 20 mL of 0.01M KCl containing P ranging from 0 to 3.223 mM P added as $KH_2PO_4$, and equilibrated in an end-over-end shaker for 24 hours at room temperature. The samples were then centrifuged at 3620 *g* for 10 min, filtered through a 0.45µm filter, and analyzed for P using the ascorbic acid method of Murphy and Riley (1962).

Anaerobic. Duplicate 1-gram samples were suspended in 10-mL of deionized water ($O_2$-free), and incubated for four weeks at room temperature. The tubes were kept anaerobic by purging the samples three times a week with pre-purified $N_2$ gas. At the end of incubation, 10 mL of graded series of P solutions in a 0.02M KCl matrix were injected into the centrifuge tubes through a rubber septum fitted into a hole drilled in the cap. The spiking P solutions were pre-calculated so that the final concentrations of P in the samples would be the same as those used for aerobic isotherms. The samples were allowed to equilibrate in an end-over-end shaker for 24 hours at room temperature, after which the tubes were centrifuged at 3620 *g* for 10 min. The supernatant liquid was withdrawn with a syringe, and filtered through a 0.45µm filter under $O_2$-free conditions. Phosphorus in solution was analyzed according to the procedure of Murphy and Riley (1962) on a Technicon Auto Analyzer II.

Phosphorus Desorption Experiments

Phosphorus desorption isotherms under aerobic and anaerobic conditions were obtained by using the same procedures outlined above for P adsorption. To produce a starting value for adsorbed P, soil samples were initially equilibrated with 20 mL of 0.01M KCl solution containing 3.223 mM P as $KH_2PO_4$. After 24-h shaking, the samples were centrifuged at 3620 *g* for 10 min, filtered through a 0.45 μm filter, and analyzed for P. The "P-saturated" soils were then subjected to sequential desorption with 20 mL of 0.01M KCl equilibrated in an end-over-end shaker for 24 hours. Sequentially desorbable P was determined by summing the total P desorbed per unit mass of soil after nine 24-h successive extractions.

Evaluation of P Sorption Data

The amount of P that disappeared from solution after 24-h equilibration represents the fraction of P sorbed by the soil. The term sorption refers here to the removal of P from the solution as a result of adsorption by the soil or by precipitation. Sorption of added P, $S_i$ (mmol P $kg^{-1}$) was calculated as follows

$$S_i = [(C_o - C_f) \times V]/w_s \qquad (3\text{-}1)$$

where $C_o$ is the initial concentration of P added (mM P), $C_f$ is the concentration of P in solution after 24-h equilibration (mM P), V is the volume of P solution added (L), and $w_s$ is the oven-dry weight of soil (kg). The parameter $S_i$ does not reflect the amount of native P initially present in the adsorbed phase ($S_n$). This value was estimated by anion-exchange resin-impregnated membrane (AEM) methodology developed by Cooperband and Logan (1994). Because resin normally extracts about half of the labile P pool, a

good measure of $S_n$ would be to multiply the resin P value by a factor of two (Fitter and Sutton, 1975). Other researchers have used 0.1M NaOH-extractable P (Ryden and Syers, 1977), isotopically exchangeable P (Holford et al., 1974), and oxalate-extractable P (Freese et al., 1992; Yuan and Lavkulich, 1994) as estimates of native sorbed P. Gale et al. (1994) used a least squares fit of $S_i$ data measured at low equilibrium P concentrations with the y-intercept representing the initial sorbed P. Preliminary evaluation of sorption data showed a generally good agreement among native sorbed P values estimated by oxalate-extraction, AEM, and least squares fit; however, the best fit of sorption data was obtained where 2x the resin P value was used. Thus, the actual amount of P adsorbed (S) at the respective equilibrium P concentration was obtained by

$$S = S_i + 2S_n \tag{3-2}$$

Sorption data were then fitted into the following equations

(i) Linearized simple Langmuir

$$C/S = (1/bS_{max}) + (C/S_{max}) \tag{3-3}$$

where C is the concentration of P remaining in solution after 24-h equilibration (mmol P $L^{-1}$), S is the total amount of P sorbed (mmol P $kg^{-1}$), b is a constant related to the bonding energy (L $mmol^{-1}$ P), and $S_{max}$ is the adsorption maximum (mmol P $kg^{-1}$). The plot of C/S versus C should yield a straight line with intercept and slope equal to $1/bS_{max}$ and $1/S_{max}$, respectively.

The maximum P buffer capacity (MBC) of the soil, which is the increase in sorbed P per unit increase in final solution P concentration, was estimated from the product of Langmuir constants (Holford and Mattingly, 1976), and is given by

$$MBC = bS_{max} \quad (3\text{-}4)$$

(ii) Linearized Freundlich

$$\log S = \log K + n \log C \quad (3\text{-}5)$$

where K is the adsorption constant, also called the partition coefficient (mmol P $kg^{-1}$), n is a constant (L $kg^{-1}$), C and S are as defined previously. A plot of logS versus logC should give a straight line with intercept and slope equal to logK and n, respectively.

It is important to note that the numerical value of K changes with the units used for S and C. If S and C have units of mmol $kg^{-1}$ and mmol $L^{-1}$, respectively, it follows that n should carry a unit of L $kg^{-1}$ in order for K to have the same unit as S. When comparing K values published in the literature, one should make sure that K carries a unit that is consistent with that of S and C. A simple way of normalizing K values with respect to proper units is described in Appendix A.

Since the Freundlich equation does not permit calculation of a sorption maximum, an alternative procedure (Yuan and Lucas, 1982) based on the non-linear regression analysis (SAS, 1985) was used to obtain the sorption maxima.

(iii) Quadratic

$$S = a_o + a_1 C + a_2 C^2 \quad (3\text{-}6)$$

where $a_o$, $a_1$, and $a_2$ are the regression coefficients, and S and C are as previously defined. The first derivation of this equation is equal to zero when S reaches the maximum,

$$dS/dC = a_1 + 2a_2 C = 0 \quad (3\text{-}7)$$

Therefore, the P concentration ($C_o$) at the adsorption maximum would be

$$C_o = C = -a_1/2a_2 \quad (3\text{-}8)$$

The sorption maximum is obtained by substituting $-a_1/2a_2$ for C in Eqn. 3-9. The equation of the plateau part of the curve describing region of maximum sorption is given as

$$S_{max} = a_o + a_1 C_o + a_2 C_o^2 \quad (3\text{-}9)$$

(iv) Temkin

$$S/S_{max} = (RT/b)\ln (AC) \quad (3\text{-}10)$$

where R is the gas constant (cal $mol^{-1}$ $deg^{-1}$), T is the absolute temperature (K), A and b are constants, and the other symbols are as defined for Eqn. 3-1. A plot of S versus lnC should give a straight line with slope equal to dS/dlnC, a term referred to as sorption index by Bache and Williams (1971).

Statistical Analyses

Data analyses were done using SAS program procedures (SAS, 1985). Adherence of the sorption data to the different adsorption models was examined using test for goodness-of-fit. Relationships among P sorption parameters were evaluated using linear correlations. Stepwise regression was used to examine the contribution of the different soil variables to P sorption and desorption behavior of soils.

## Results and Discussion

### Physico-chemical Properties of the Soils

The spodic samples contained predominantly sand-size particles. The clay fraction in the soil ranged from 1.6 to 9.9% and was dominated by quartz mineralogy

(Table 3-1). Secondary minerals such as montmorillonite, kaolinite, and hydroxy-interlayered vermicullite were present in variably low amounts in most soils.

The soils were very acidic (Table 3-2). Soil pH values in 1M KCl were lower than those measured in water indicating that all soils at their natural pHs are negatively charged. On a whole soil basis, the net negative surface charge of the spodic samples ranged from -4.10 to -30.45 mmol $kg^{-1}$ (Table 3-2). Results of the electrochemical studies presented in Chapter 2 show that the colloidal fraction of the spodic horizons was dominated by constant potential minerals whose charge varied with pH and electrolyte concentration of the soil solution. Iron and Al oxides along with organic matter dominated the charge properties of these soils. The soils had very low capacity to retain cations under field conditions. The average effective CEC of the soils excluding Vero soil, was 2.08 $cmol_{(+)}kg^{-1}$. This is not difficult to understand considering the soils are predominantly sand. Organic carbon content of the soils varied from 7.3 to 32.6 g $kg^{-1}$. These numbers were comparable to those reported for spodic horizons of soils from New York (Laverdiere and Weaver, 1977) and British Columbia, Canada (Yuan and Lavkulich, 1994). Except for Vero, the soils were dominated by Al. The mole ratio of total Al to Fe ranged from 1.2 to 42.7. Average total Al and Fe contents of the soils were 153 and 16 mmol $kg^{-1}$, respectively.

A large fraction of Al and Fe in the spodic horizon was extracted by acid oxalate reagent. This amorphous form of Fe and Al comprised a combined average of over 60% of the total Al and Fe in the soils (Table 3-3). The spodic horizons from Southern New Zealand (Parfitt and Childs, 1988), Canada (Yuan and Lavkulich, 1994; Wang et al.,

Table 3-1. Location, mineralogy, and taxonomic classification of the spodic horizons used in the study. Data were obtained from the soil survey reports prepared jointly by the University of Florida Soil and Water Science Department and the USDA Soil Conservation Service.

| Soil Series | County | Depth, cm | Clay, % | Mineralogy[¶] | Taxonomic Group |
|---|---|---|---|---|---|
| Cornelia | Duval | 99-112 | 9.9 | MT>QZ>>KL>HIV | Arenic Haplorthods |
| EauGallie | Highlands | 66-84 | 4.7 | QZ>MT>>KL | Alfic Arenic Alaquods |
| Immokalee | Flagler | 109-137 | 2.4 | KL>QZ>HIV | Aeric Alaquods |
| Kingsferry | Nassau | 170-203 | 2.2 | QZ>>>KL>HIV | Arenic Alaquods |
| Leon | Baker | 43-58 | 5.0 | No Data | Aeric Alaquods |
| Myakka | Sumter | 64-79 | 1.7 | QZ>HIV>KL>MT | Aeric Alaquods |
| Narcoose | Polk | 43-48 | 3.3 | QZ>>MT>HIV>KL | Entic Haplorthods |
| Oldsmar | Highlands | 89-109 | 3.4 | QZ>>MT>KL>HIV | Alfic Arenic Alaquods |
| Ona | Hardee | 23-41 | 5.1 | QZ | Arenic Alaquods |
| Pomello | St. Johns | 114-130 | 3.6 | QZ | Arenic Haplorthods |
| Pomona | St. Johns | 55-58 | 3.9 | QZ>>HIV>>KL | Ultic Alaquods |
| Sapelo | Clay | 46-58 | 4.0 | QZ>HIV>>KL | Ultic Alaquods |
| Smyrna | Desoto | 188-203 | 1.6 | QZ>>MT>HIV>KL | Aeric Alaquods |
| Vero | Osceola | 61-71 | 6.0 | QZ>>>MT>HIV>FD>KL | Alfic Alaquods |
| Wabasso | Martin | 58-91 | 2.0 | QZ>>>MT>KL | Alfic Alaquods |
| Wauchula | Alachua | 46-58 | 7.3 | QZ>>>HIV>KL | Ultic Alaquods |

¶ Arranged in relative order of abundance.

MT-montmorillonite; HIV-hydroxy interlayered vermicullite; KL-kaolinite; QZ-quartz; FD-feldspar.

Table 3-2. Selected chemical properties of the spodic horizons used in the study.

| Soil Series | $pH_{H2O}$ | $pH_{KCl}$ | Exchangeable Bases, $mmol_{(+)}\ kg^{-1}$ | | | | | Exch. Al $mmol_{(+)}\ kg^{-1}$ | ECEC[¶] $cmol_{(+)}\ kg^{-1}$ | Net Surface Charge $mmol\ kg^{-1}$ | Org. C $g\ kg^{-1}$ | Total, $mmol\ kg^{-1}$ | | Al:Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ca | Mg | K | Na | Σ Bases | | | | | Al | Fe | |
| Cornelia | 4.07 | 3.15 | 8.25 | 2.33 | 0.38 | 1.29 | 12.25 | 11.94 | 2.42 | -16.20 | 13.2 | 139.27 | 65.58 | 2.12 |
| EauGallie | 4.29 | 3.42 | 1.92 | 2.84 | 0.28 | 0.74 | 5.78 | 17.03 | 2.28 | -11.55 | 14.9 | 32.15 | 16.04 | 2.00 |
| Immokalee | 5.34 | 4.39 | 0.81 | 1.34 | 0.26 | 0.54 | 2.95 | 22.63 | 2.56 | -14.25 | 20.4 | 47.54 | 2.40 | 19.80 |
| Kingsferry | 4.33 | 3.98 | 0.40 | 0.51 | 0.26 | 0.35 | 1.52 | 6.10 | 0.76 | -4.10 | 32.1 | 465.68 | 13.66 | 34.09 |
| Leon | 4.11 | 3.54 | 1.38 | 0.67 | 0.31 | 0.52 | 2.88 | 18.96 | 2.19 | -8.05 | 21.1 | 139.33 | 3.67 | 37.96 |
| Myakka | 4.11 | 3.15 | 1.67 | 1.45 | 0.32 | 0.47 | 3.91 | 17.59 | 2.15 | -15.05 | 24.7 | 83.28 | 3.81 | 21.86 |
| Narcoose | 4.23 | 3.17 | 1.19 | 2.88 | 1.56 | 1.04 | 6.67 | 6.74 | 1.34 | -6.62 | 14.4 | 94.02 | 3.94 | 23.86 |
| Oldsmar | 3.96 | 2.99 | 1.11 | 1.57 | 0.28 | 0.55 | 3.51 | 13.93 | 1.74 | -11.93 | 32.6 | 119.99 | 4.08 | 29.41 |
| Ona | 4.86 | 3.86 | 25.49 | 6.38 | 6.32 | 0.42 | 38.61 | 3.93 | 4.25 | -30.45 | 26.1 | 248.81 | 6.74 | 36.92 |
| Pomello | 4.20 | 3.42 | 0.62 | 0.67 | 0.28 | 0.38 | 1.95 | 9.07 | 1.10 | -6.11 | 15.3 | 53.76 | 1.26 | 42.67 |
| Pomona | 4.37 | 3.83 | 1.12 | 0.85 | 0.29 | 0.57 | 2.83 | 16.73 | 1.96 | -7.82 | 25.1 | 381.14 | 18.43 | 20.68 |
| Sapelo | 3.62 | 3.33 | 1.08 | 0.84 | 0.29 | 0.43 | 2.64 | 21.81 | 2.44 | -13.06 | 16.2 | 85.92 | 4.62 | 18.60 |
| Smyrna | 4.62 | 4.34 | 1.09 | 1.14 | 0.26 | 0.50 | 2.99 | 4.58 | 0.76 | -1.20 | 7.3 | 260.97 | 6.67 | 39.13 |
| Vero | 6.29 | 5.46 | 35.71 | 44.19 | 0.98 | 22.09 | 102.97 | 0.19 | 10.31 | -21.79 | 15.1 | 67.03 | 75.86 | 0.88 |
| Wabasso | 5.23 | 4.48 | 21.40 | 4.06 | 0.28 | 2.20 | 27.94 | 0.85 | 2.88 | -13.23 | 8.6 | 19.39 | 16.72 | 1.16 |
| Wauchula | 4.57 | 3.82 | 1.70 | 0.67 | 0.28 | 0.44 | 3.09 | 21.37 | 2.45 | -11.16 | 19.9 | 208.67 | 4.84 | 43.11 |

[¶]ECEC- effective cation exchange capacity.

Table 3-3. The forms of aluminum and iron in the spodic horizons. (k is potassium chloride; c is cupric chloride; p is sodium pyrophosphate; o is ammonium oxalate; d is citrate-dithionite-bicarbonate).

| Soil Serie | Extractable Al , mmol kg$^{-1}$ | | | | | Extractable Fe , mmol kg$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Al_k$ | $Al_c$ | $Al_p$ | $Al_o$ | $Al_d$ | $Fe_p$ | $Fe_o$ | $Fe_d$ | $(Al+Fe)_o$ | $(Al+Fe)_p$ | $Fe_d$-$Fe_o$[¶] |
| Cornelia | 3.98 | 27.52 | 53.26 | 52.49 | 56.36 | 38.09 | 49.74 | 56.56 | 91.35 | 102.23 | 6.82 |
| EauGallie | 5.68 | 18.19 | 22.06 | 23.74 | 24.97 | 12.20 | 15.25 | 15.35 | 34.26 | 39.09 | 0.10 |
| Immokalee | 7.55 | 31.93 | 40.00 | 38.65 | 46.72 | 0.26 | 0.14 | 0.81 | 40.26 | 38.79 | 0.67 |
| Kingsferry | 2.04 | 68.00 | 354.96 | 337.56 | 254.96 | 1.19 | 0.22 | 0.70 | 356.15 | 337.78 | 0.48 |
| Leon | 6.33 | 37.29 | 75.91 | 82.16 | 99.98 | 0.58 | 0.66 | 0.96 | 76.49 | 82.82 | 0.30 |
| Myakka | 5.87 | 38.26 | 56.45 | 50.35 | 57.88 | 1.00 | 0.68 | 1.12 | 57.45 | 51.03 | 0.44 |
| Narcoose | 2.25 | 10.13 | 44.44 | 44.18 | 55.90 | 1.27 | 1.31 | 1.65 | 45.71 | 45.49 | 0.34 |
| Oldsmar | 4.65 | 21.33 | 71.75 | 68.67 | 88.62 | 1.18 | 1.01 | 1.24 | 72.93 | 69.68 | 0.23 |
| Ona | 1.32 | 23.09 | 166.80 | 168.59 | 223.63 | 2.95 | 3.14 | 4.93 | 169.75 | 171.73 | 1.79 |
| Pomello | 3.03 | 17.07 | 42.90 | 46.02 | 48.57 | 0.21 | 0.20 | 0.38 | 43.11 | 46.22 | 0.18 |
| Pomona | 5.58 | 140.01 | 265.61 | 258.48 | 265.51 | 5.81 | 3.11 | 5.79 | 271.42 | 261.59 | 2.68 |
| Sapelo | 7.27 | 28.64 | 44.12 | 44.40 | 52.57 | 1.39 | 1.52 | 1.61 | 45.51 | 45.92 | 0.09 |
| Smyrna | 1.53 | 78.01 | 180.61 | 153.67 | 133.13 | 2.19 | 0.72 | 1.19 | 182.80 | 154.39 | 0.47 |
| Vero | 0.06 | 10.23 | 24.02 | 20.39 | 41.19 | 18.18 | 11.84 | 72.07 | 42.20 | 32.23 | 60.23 |
| Wabasso | 0.29 | 9.11 | 13.91 | 13.34 | 12.85 | 13.63 | 12.87 | 16.66 | 27.54 | 26.21 | 3.79 |
| Wauchula | 7.13 | 118.48 | 167.89 | 161.55 | 168.68 | 1.81 | 1.43 | 2.17 | 169.70 | 162.98 | 0.74 |

[¶] Estimate of Fe in goethite and hematite.

1987), and northeastern U.S. (Laverdiere and Karam, 1977) have been reported to contain Fe and Al largely in amorphous form, except that the mole ratios of Al to Fe in these soils were much lower, suggesting greater accumulation of Fe in these soils than in Florida Spodosols. The fraction of Al and Fe that dissolved in pyrophosphate solution was equally high. Pyrophosphate is known to extract Al and Fe organic complexes while, oxalate dissolves both amorphous and organically bound Fe and Al (Parfitt and Childs, 1988). The difference between the two extractions is taken to represent the amount of amorphous inorganic Fe and Al oxides (McKeague et al., 1971). However, in this study the extractability of both reagents was very similar, indicating that pyrophosphate could be extracting more than just the organo-metallic complexes. Zhou (1994) reported the same findings for the five of eight Bh samples he studied. Cupric chloride is another reagent used to extract Al associated with organic matter. By comparison, this reagent gave values much lower than pyrophosphate, which indicates the lack of selectivity of the pyrophosphate reagent. The values obtained from CDB extraction [$(Al+Fe)_d$] were as large as oxalate. This was not surprising considering that CDB reagent is less selective than acid oxalate reagent. CDB solubilizes a large portion of both crystalline and amorphous forms of Al and Fe. Thus, to obtain a realistic estimate of the amount of crystalline forms of Al and Fe in the soil, the convention is to take the difference between CDB and oxalate extractions (Freese et al., 1992). Compared to oxalate and pyrophosphate extractable Al and Fe, this fraction accounted for a very small portion of the total Al and Fe in the soils. The difference between CDB and oxalate-extractable Fe ($Fe_d$-$Fe_o$) has been used as a quantitative estimate of Fe in goethite and hematite (Parfitt

and Childs, 1988). Relative to the total Fe content of the soils, this crystalline form of Fe in the soils was low, except for Fe-dominated Vero soil. Exchangeable Al, that fraction of Al that dissolves in potassium chloride was the smallest of the pools. This form of Al is considered to be the most reactive. One $cmol_{(+)}$ of exchangeable Al when hydrolyzed may fix up to 3.3 mmol P per kg of soil (Sanchez and Uehara, 1980).

Phosphorus originally present in the soils was largely in the form of inorganic Fe/Al-P ($NaOH\text{-}P_i$). The fraction accounted for an average of over 35% of the total P (Table 3-4). Another 30% was accounted for by P associated with organic matter ($NaOH\text{-}P_o$). These numbers suggest that Fe and Al are the main components reacting with P in the spodic horizon.

Phosphorus Sorption Behavior

As pointed out earlier, the spodic horizons used in this study cover a wide range of Al and Fe levels commonly found in Florida Spodosols. Thus, any specific pattern of P sorption behavior depicted by the soils would likely be a reflection of their Fe and Al contents. In view of the wide differences in the total Al and Fe content of the soils, it was decided to separate the soils into different groups that would allow meaningful comparison and interpretation of the P sorption parameters. Since the spodic horizons were Al-dominated, the soils were grouped based on their total Al content. The spodic samples were arbitrarily categorized into low-Al, medium-Al, and high-Al soils. The soils belonging to each group are listed in Table 3-5. The average total Al content of the soils were 44, 132, and 313 mmol $kg^{-1}$, respectively. The corresponding Fe content of

Table 3-4. Distribution of the different P fractions in the spodic horizons. Numbers in parentheses are P fractions expressed as percent of total P.

| Soil | P Fraction, mmol $kg^{-1}$ of soil | | | | | |
|---|---|---|---|---|---|---|
| | $NH_4Cl$-P | NaOH-$P_i$ | NaOH-$P_o$ | HCl-P | Residual P[§] | Total P |
| Cornelia | 0.03 (0.1) | 24.25 (66.8) | 4.99 (13.8) | 0.40 ( 1.1) | 6.62 (18.2) | 36.29 |
| EauGallie | 0.00 (0.0) | 0.40 (28.5) | 0.41 (29.1) | 0.01 ( 0.4) | 0.59 (41.9) | 1.40 |
| Immokalee | 0.00 (0.0) | 0.07 ( 3.2) | 0.16 ( 7.7) | 0.00 ( 0.2) | 1.81 (88.9) | 2.04 |
| Kingsferry | 0.00 (0.0) | 4.37 (53.5) | 0.93 (11.3) | 0.04 ( 0.5) | 2.84 (34.7) | 8.18 |
| Leon | 0.00 (0.0) | 0.35 (11.5) | 1.85 (60.9) | 0.03 ( 1.0) | 0.81 (26.6) | 3.03 |
| Myakka | 0.00 (0.0) | 1.39 (34.0) | 2.03 (49.7) | 0.02 ( 0.5) | 0.64 (15.8) | 4.08 |
| Narcoose | 0.14 (0.5) | 4.85 (52.3) | 2.59 (27.9) | 0.02 ( 0.2) | 1.67 (18.0) | 9.27 |
| Oldsmar | 0.00 (0.0) | 2.03 (56.8) | 0.71 (20.0) | 0.02 ( 0.6) | 0.81 (22.6) | 3.57 |
| Ona | 0.91 (1.3) | 56.98 (80.3) | 8.66 (12.2) | 0.40 ( 0.6) | 4.03 ( 5.7) | 70.98 |
| Pomello | 0.00 (0.0) | 0.20 (11.2) | 0.89 (48.5) | 0.01 ( 0.2) | 0.74 (40.2) | 1.83 |
| Pomona | 0.00 (0.0) | 0.22 ( 5.6) | 1.23 (32.0) | 0.01 ( 0.2) | 2.38 (62.2) | 3.83 |
| Sapelo | 0.00 (0.0) | 0.13 ( 6.5) | 0.84 (43.5) | 0.01 ( 0.3) | 0.97 (49.7) | 1.94 |
| Smyrna | 0.00 (0.0) | 9.21 (88.0) | 2.32 (22.2) | 0.04 ( 0.4) | 1.90 (14.1) | 13.47 |
| Vero | 0.00 (0.0) | 0.12 ( 5.6) | 0.47 (21.5) | 0.00 ( 0.1) | 1.57 (72.8) | 2.16 |
| Wabasso | 0.00 (0.0) | 0.60 ( 9.2) | 0.10 (15.7) | 0.00 ( 0.3) | 0.49 (74.8) | 0.65 |
| Wauchula | 0.00 (0.0) | 0.18 ( 7.3) | 1.15 (45.9) | 0.01 ( 0.2) | 1.17 (46.7) | 2.51 |

[§] Obtained by taking the difference between total P and the sum of all P fractions.

Table 3-5. Grouping of soils based on their total Al content.

| Soil | Total Al | Total Fe | Total Al+Fe |
|---|---|---|---|
| | ---------- mmol $kg^{-1}$ ---------- | | |
| I. Low-Al | | | |
| EauGallie | 32.15 | 16.04 | 48 |
| Immokalee | 47.54 | 2.40 | 50 |
| Pomello | 53.76 | 1.26 | 55 |
| Vero | 67.03 | 75.86 | 143 |
| Wabasso | 19.39 | 16.72 | 36 |
| | **43.97**[§] | **22.46** | **66** |
| II. Medium-Al | | | |
| Cornelia | 139.27 | 65.68 | 205 |
| Leon | 139.33 | 3.67 | 143 |
| Myakka | 83.28 | 3.81 | 87 |
| Narcoose | 94.02 | 3.94 | 98 |
| Oldsmar | 119.99 | 4.08 | 124 |
| Sapelo | 85.92 | 4.62 | 90 |
| | **132.36** | **17.14** | **150** |
| III. High-Al | | | |
| Kingsferry | 465.68 | 13.66 | 479 |
| Ona | 248.81 | 6.74 | 256 |
| Pomona | 381.14 | 18.43 | 400 |
| Smyrna | 260.97 | 6.67 | 268 |
| Wauchula | 208.67 | 4.84 | 214 |
| | **313.05** | **10.07** | **323** |

[§] Mean values.

the soils were 22, 17, and 10 mmol $kg^{-1}$. This resulted in a combined Al and Fe content of 66, 150, and 323 mmol $kg^{-1}$ for low-, medium-, and high-Al soils, respectively.

Phosphorus sorption isotherms. The Al-grouping effectively separated the spodic horizons with respect to their P sorption capacity (Fig. 3-3). Low-Al soils were characterized by flat curves with sorption not exceeding 10 mmol P $kg^{-1}$ at any point on the isotherm. Sorption curves for medium-Al soils were slightly steeper, but were more variable compared to low-Al soils. High-Al soils exhibited the largest capacity to sorb P that varied widely from soil to soil. Sorption at the highest level of P added (3.223mM P) ranged from below 10 to as high as 30 mmol P $kg^{-1}$. The slope of the sorption curves was generally steeper for aerobic than anaerobic soils, implying reduced P sorption upon flooding.

The P sorption data were plotted according to the linear Langmuir, Freundlich, Temkin, and quadratic equations. Graphical representations of these isotherms for representative soil samples are shown in Fig. 3-4 to 3-7. In general, the simple Langmuir equation gave the best fit of the sorption data. At least for the three soils depicted in Fig. 3-4, the relationship between C/S and S was linear up to P concentration of 3.223 mM P. This suggests that the assumption of constant binding energy inherent in the Langmuir equation holds true for these soils. This is quite surprising for a system as heterogeneous and as complex as the spodic horizon. Rajan and Fox (1975) obtained similar sorption energy for populations of sites which they established for very different soils. Mehadi and Taylor (1988) reported a near perfect fit of their P sorption data with the linear form of the Langmuir equation. The fit of P sorption data according to Freundlich equation

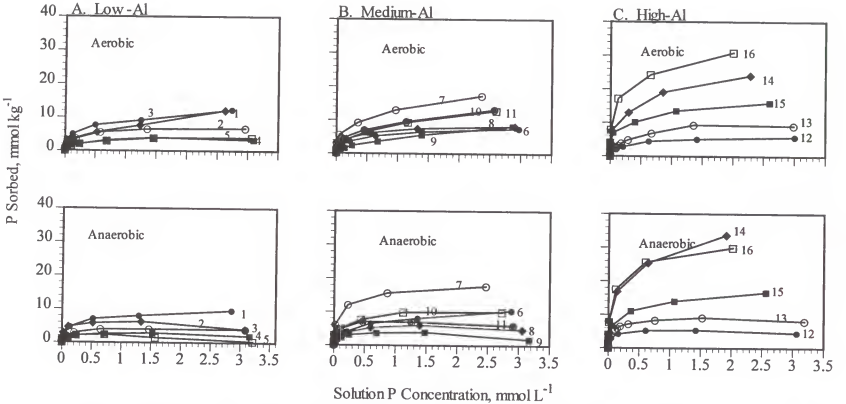



Fig. 3-3. Direct plot of P sorption for low, medium, and high-Al soils under aerobic and anaerobic conditions. 1-EauGallie; 2-Immokalee; 3-Pomello; 4-Vero; 5-Wabasso; 6- Cornelia; 7-Leon; 8-Myakka; 9-Narcoose; 10-Oldsmar; 11-Sapelo; 12-Kingsferry; 13-Ona; 14-Pomona; 15-Smyrna; 16-Wauchula.

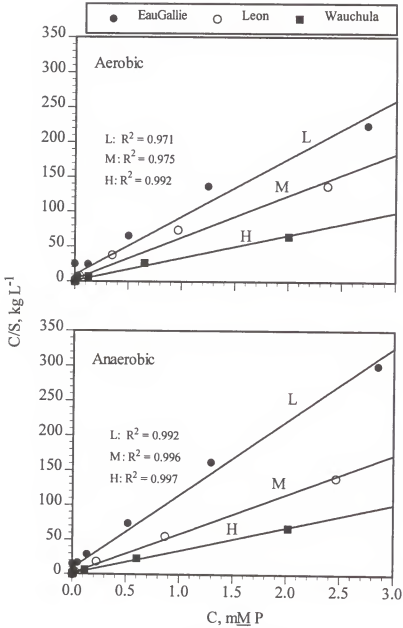



Fig. 3-4. Graphical representation of the linear Langmuir isotherm for some representative samples. L is low-Al; M is medium-Al; H is high-Al.

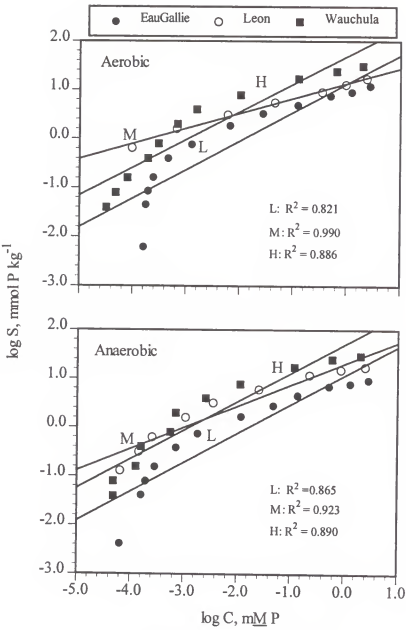



Fig. 3-5. Graphical representation of the linear Freundlich isotherm for some representative samples. L is low-Al; M is medium-Al; H is high-Al.

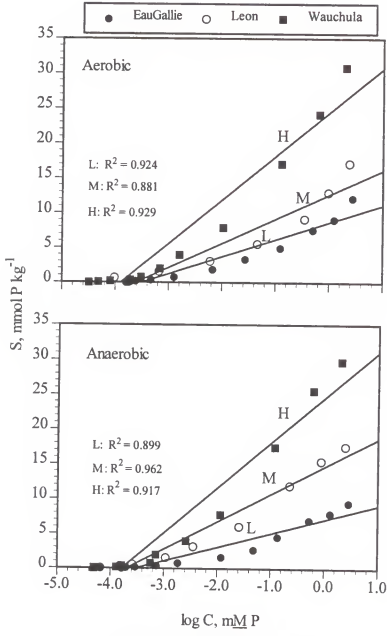



Fig. 3-6. Graphical representation of the Temkin isotherm for some representative samples. L is low-Al; M is medium-Al; H is high-Al.

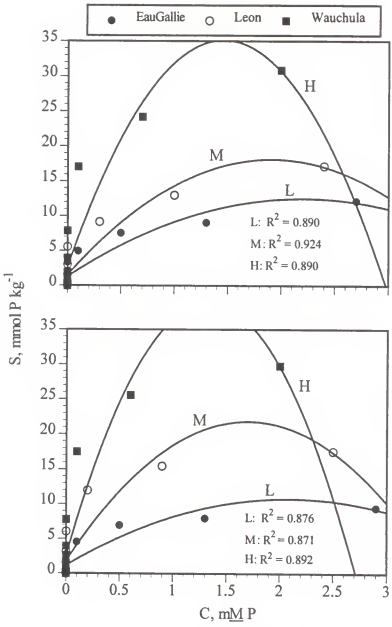



Fig. 3-7. Graphical representation of the quadratic isotherm for some representative samples. L is low-Al; M is medium-Al; H is high-Al.

was not as good (Fig. 3-5). The relationship between log S and log C deviated from linearity at low P concentrations. However, at higher equilibrium P concentrations, the equation yielded a linear relationship that is consistent with a number of independent observations (Polyzopoulos et al., 1985; Ratkowsky, 1986; Sanyal et al., 1993). The Langmuir-derived Temkin equation produced gentle curves rather than straight lines (Fig. 3-6). Such behavior was also reported by several researchers (Roy and De Datta, 1985; Russell et al., 1988; Sanyal et al., 1993). Relative to the other models, the quadratic fit of the sorption data was the weakest (Fig. 3-7). Berkheiser et al. (1980), however, reported an excellent fit of their P sorption data with the quadratic equation.

The goodness-of-fit of the four adsorption equations was compared by simple linear regression analyses. Regression coefficients of 0.90 or better are considered very good fits. Irrespective of the grouping and soil condition, the Langmuir equation gave the best fit of the sorption data (Table 3-6). Overall regression coefficients were 0.98±0.03, 0.90±0.07, 0.91±0.06, and 0.89±0.06 for Langmuir, Freundlich, Temkin and quadratic models, respectively. Breaking the soils down into the different groups, P sorption data for medium- and high-Al soils conformed to the adsorption equations better than low-Al soils did. However, mean regression coefficients for Freundlich and quadratic equations were lower for anaerobic (0.86± 0.06) than aerobic soils (0.92±0.04). This can be attributed to changes in properties of P-sorbing surfaces brought about by flooding.

Table 3-6. Correlation coefficients ($R^2$) describing the goodness-of-fit of the four isotherm models on P sorption data.

| Soil | Aerobic | | | | Anaerobic | | | |
|---|---|---|---|---|---|---|---|---|
| | Langmuir | Freundlich | Temkin | Quadratic | Langmuir | Freundlich | Temkin | Quadratic |
| I. Low-Al | | | | | | | | |
| EauGallie | 0.971 | 0.821 | 0.924 | 0.890 | 0.992 | 0.865 | 0.899 | 0.876 |
| Immokalee | 0.982 | 0.842 | 0.893 | 0.889 | 0.997 | 0.867 | 0.857 | 0.814 |
| Pomello | 0.922 | 0.985 | 0.788 | 0.940 | 0.975 | 0.852 | 0.850 | 0.709 |
| Vero | 0.991 | 0.964 | 0.880 | 0.914 | 0.975 | 0.925 | 0.878 | 0.809 |
| Wabasso | 0.991 | 0.744 | 0.875 | 0.923 | 0.864 | 0.722 | 0.731 | 0.784 |
| II. Medium-Al | | | | | | | | |
| Cornelia | 0.996 | 0.938 | 0.995 | 0.933 | 0.985 | 0.982 | 0.974 | 0.954 |
| Leon | 0.975 | 0.990 | 0.881 | 0.924 | 0.996 | 0.923 | 0.962 | 0.871 |
| Myakka | 0.998 | 0.920 | 0.974 | 0.888 | 0.984 | 0.892 | 0.923 | 0.856 |
| Narcoose | 0.912 | 0.994 | 0.868 | 0.992 | 0.929 | 0.817 | 0.875 | 0.834 |
| Oldsmar | 0.961 | 0.975 | 0.886 | 0.959 | 0.998 | 0.945 | 0.973 | 0.906 |
| Sapelo | 0.963 | 0.995 | 0.879 | 0.926 | 0.996 | 0.910 | 0.924 | 0.838 |
| III. High-Al | | | | | | | | |
| Kingsferry | 0.992 | 0.934 | 0.912 | 0.882 | 0.995 | 0.896 | 0.940 | 0.824 |
| Ona | 0.994 | 0.944 | 0.975 | 0.980 | 0.995 | 0.839 | 0.847 | 0.910 |
| Pomona | 0.985 | 0.949 | 0.906 | 0.927 | 0.987 | 0.815 | 0.952 | 0.916 |
| Smyrna | 0.991 | 0.897 | 0.972 | 0.878 | 0.992 | 0.805 | 0.959 | 0.884 |
| Wauchula | 0.992 | 0.886 | 0.929 | 0.890 | 0.997 | 0.890 | 0.917 | 0.892 |
| Grand Mean | 0.976 | 0.924 | 0.909 | 0.921 | 0.993 | 0.849 | 0.923 | 0.885 |
| Std Deviation | ±0.036 | ±0.029 | ±0.033 | ±0.035 | ±0.063 | ±0.063 | ±0.060 | ±0.060 |

Phosphorus sorption parameters. The spodic horizons in general are characterized by low EPC values that are consistent with the resin-P values (Table 3-7). Equilibrium P concentration (EPC) represents the P in solution that is in equilibrium with P in the solid phase. In theory, it is the solution P concentration at which the amount of P sorbed (uncorrected) intersects the abcissa (x-intercept) in the S versus C plot (McCallister and Logan, 1978). Excluding the high P-containing Cornelia, Narcoose, and Ona, the mean EPC values of the soils was 0.3 μM P for aerobic soils and 0.4 μM P for anaerobic soils. These values were comparable to those reported by Nair et al. (1997) for spodic horizons from the native, unimpacted areas in the Lake Okeechobee watershed but were much lower than those found for manure-impacted soils in the nearby areas. An important application of EPC lies in the prediction of P movement across the soil/sediment-water interface (Logan and McLean, 1973; McCallister and Logan, 1978). The low EPC values associated with the spodic horizons used in the study, suggest that these soils are likely to act as sinks for P. The Langmuir sorption maxima ($S_{max}$) of the spodic horizons ranged from 3.93 to 30.65 mmol P $kg^{-1}$ with a mean value of 11.98 mmol P $kg^{-1}$ (Table 3-8). These values agree with those obtained by Nair et al. (1997) and Zhou (1994) for several Bh horizons in Florida, but were much lower than the values obtained for forty three spodic samples from British Columbia (Yuan and Lavkulich, 1994) and six spodic samples from Northeastern U.S. and Canada (Laverdiere, 1982). A mean $S_{max}$ value of 54 mmol P $kg^{-1}$ was reported for these soils. It should be noted however, that the Canadian soils contained considerably higher levels of Fe and Al and twice as much clay as the Florida soils.

Table 3-7. Resin-P and EPC values for the spodic horizons under aerobic and anaerobic conditions.

| Soil | Aerobic | | Anaerobic | |
|---|---|---|---|---|
| | EPC μM P | Resin-P μmol $g^{-1}$ | EPC μM P | Resin-P μmol $g^{-1}$ |
| I. Low-Al | | | | |
| EauGallie | 0.1 | 0.00 | 0.1 | 0.00 |
| Immokalee | 0.1 | 0.00 | 0.3 | 0.00 |
| Pomello | 0.0 | 0.01 | 0.1 | 0.00 |
| Vero | 0.0 | 0.00 | 1.2 | 0.00 |
| Wabasso | 0.0 | 0.00 | 0.1 | 0.00 |
| II. Medium-Al | | | | |
| Cornelia | 29.3 | 0.39 | 23.0 | 0.54 |
| Leon | 0.0 | 0.00 | 0.0 | 0.00 |
| Myakka | 1.8 | 0.07 | 1.6 | 0.05 |
| Narcoose | 47.6 | 0.51 | 37.3 | 0.67 |
| Oldsmar | 1.2 | 0.10 | 2.0 | 0.17 |
| Sapelo | 0.1 | 0.01 | 0.1 | 0.00 |
| III. High-Al | | | | |
| Kingsferry | 0.0 | 0.00 | 0.0 | 0.00 |
| Ona | 194.6 | 2.09 | 24.1 | 3.57 |
| Pomona | 0.0 | 0.00 | 0.1 | 0.00 |
| Smyrna | 0.1 | 0.00 | 0.1 | 0.00 |
| Wauchula | 0.0 | 0.00 | 0.0 | 0.00 |

Table 3-8. Phosphorus sorption parameters for the spodic horizons obtained from the linear Langmuir equation. $S_{max}$ is P sorption maximum; b is a constant related to P binding energy; MBC is maximum buffer capacity.

| Soil | Aerobic | | | Anaerobic | | |
|---|---|---|---|---|---|---|
| | $S_{max}$ mmol P $kg^{-1}$ | b L $mmol^{-1}$ P | MBC L $kg^{-1}$ | $S_{max}$ mmol P $kg^{-1}$ | b L $mmol^{-1}$ P | MBC L $kg^{-1}$ |
| I. Low-Al | | | | | | |
| EauGallie | 11.85 | 11.5 | 136 | 9.92 | 11.8 | 117 |
| Immokalee | 6.80 | 14.2 | 96 | 4.26 | 19.8 | 84 |
| Pomello | 11.17 | 8.4 | 94 | 6.20 | 83.4 | 518 |
| Vero | 3.93 | 13.1 | 51 | 2.72 | 21.0 | 56 |
| Wabasso | 4.00 | 10.5 | 42 | 2.41 | 44.0 | 106 |
| | **7.55** [§] | **11.5** | **84** | **5.10** | **36.0** | **176** |
| II. Medium-Al | | | | | | |
| Cornelia | 7.85 | 4.7 | 37 | 10.63 | 4.7 | 49 |
| Leon | 16.65 | 20.1 | 333 | 17.54 | 39.5 | 695 |
| Myakka | 8.33 | 8.5 | 71 | 6.25 | 10.6 | 66 |
| Narcoose | 8.39 | 2.6 | 22 | 3.98 | 13.8 | 55 |
| Oldsmar | 12.68 | 6.2 | 79 | 10.12 | 14.1 | 142 |
| Sapelo | 12.58 | 13.2 | 166 | 7.23 | 84.9 | 613 |
| | **11.08** | **9.2** | **118** | **9.29** | **27.9** | **270** |
| III. High-Al | | | | | | |
| Kingsferry | 5.66 | 14.7 | 83 | 5.56 | 53.5 | 297 |
| Ona | 11.81 | 2.5 | 30 | 9.49 | 10.9 | 103 |
| Pomona | 23.61 | 20.1 | 472 | 33.72 | 16.0 | 539 |
| Smyrna | 15.71 | 18.4 | 287 | 16.38 | 18.7 | 301 |
| Wauchula | 30.65 | 27.8 | 852 | 29.96 | 30.0 | 896 |
| | **17.49** | **16.7** | **345** | **19.02** | **25.8** | **427** |

[§] Mean values.

The spodic horizons exhibited P sorption capacities that were consistent with their total Al content. Mean $S_{max}$ values of 7.55, 11.08, and 17.49 mmol P $kg^{-1}$ were obtained for low-, medium-, and high-Al soils, respectively (Table 3-8). Flooding altered the P sorption capacity of the soils. The effect however, was inconsistent from soil to soil within each of the three soil groups. Flooding decreased the P sorption capacity of the low- and medium-Al soils, but slightly increased that of high-Al soils. Nair et al. (pers. commun.) reported substantial reduction in P sorption capacities under anaerobic conditions, of several spodic horizons from Spodosols in the Lake Okeechobee basin. In acid soils, reduction in P sorption upon flooding is generally attributed to increased levels of solution P via reductive dissolution of Al and Fe phosphates (Ponnamperuma, 1972; Willett, 1986). Also, the rise in pH that accompanies soil reduction would tend to reduce the surface positive charge on soils causing desorption of P from clay, and Al and Fe oxide surfaces (Tian-ren et al., 1989; Willett, 1989). The increased P sorption in high-Al soils can be attributed to the pH-induced adsorption of P by Al-organo complexes (Bloom, 1981) and to the formation of amorphous Al-hydroxy-phosphates (Veith and Sposito, 1977; Bloom, 1981). Haynes and Swift (1989) showed that Al-organic matter associations had a high P sorption capacity that increased with pH.

The Langmuir constant b, the parameter that defines the energy of adsorption of P to the soil surface gave values that were consistent with the native P content of the soils. Within a given soil group, b values were smaller for soils high in native P (Table 3-4; 3-8). Ona, for example the soil with the lowest b value of 2.5 L $mmol^{-1}$ P had a total P content of over 70 mmol P $kg^{-1}$. By comparison, Wauchula whose b value was the

largest (27.8 L $mmol^{-1}$ P) had just over 2 mmol P $kg^{-1}$ total P. Mehadi and Taylor (1988) reported smaller b values for cultivated soils than the virgin soils. They explained their findings in terms of the saturation of the sorption complex or more specifically, the number of sites available for further sorption. For a soil with only a small proportion of the total adsorption sites occupied, as was the case for the virgin soils, the sites are more active and have greater heats of adsorption which translate into higher energies of binding. Agbenin and Tiessen (1994) offered a similar explanation for the low b values associated with the P-laden semiarid soils from Brazil. According to Watanabe and Olsen (1957), b is equivalent to the reciprocal of the equilibrium P concentration when one-half of the total sites are occupied. Contrary to the results reported by Nair et al. (pers. commun.) for the spodic horizons from Spodosols in south Florida, flooding markedly increased the b values of the soils. One would expect that reduced P sorption would result in lower b values, but such was not the case for the spodic horizons used in this study. Several researchers (Willett, 1979, 1982; Sah and Mikkelsen, 1986a, 1986b) attributed increased energy of adsorption upon flooding to increased activity of Fe oxides in sorbing P.

The maximum buffer capacity (MBC) is a qualitative or intensive parameter describing the resistance to change of the P concentration in the soil solution or the labile solid phase (Holford, 1979). It is the product of Langmuir adsorption maximum ($S_{max}$) and the bonding energy term (b), and it can be calculated from the equation

$$S = S_{max} bC/(1 + bC) \qquad (3\text{-}11)$$

On differentiating with respect to C, the Langmuir equation becomes

$$dS/dC = S_{max}b/(1 + bC)^2 \qquad (3\text{-}12)$$

The maximum buffering capacity, MBC (L $kg^{-1}$) is obtained as C approaches zero. The MBC values of the soils are consistent with their P sorption capacities. High MBC values were associated with high P-sorbing soils such as Leon, Pomona, Smyrna, and Wauchula. High MBC values generally indicate very low concentrations of P in solution. Thus, the mobility of P in soils such as Wabasso or Vero would be greater than any of the spodic horizons mentioned above. Increased buffer capacity due to flooding has been attributed to P sorption from soil solution by the reprecipitated poorly crystalline ferrous hydroxides (Patrick et al., 1985; Tian-ren et al., 1989).

The Freundlich adsorption coefficient, K of the soils varied widely. The parameter K has been used as a measure of relative P sorption capacity of soils (Biggar and Cheung, 1973; Sanyal and De Datta, 1993). Without pertaining to any particular grouping, the K values ranged between 3.5 and 47.8 mmol P $kg^{-1}$ (Table 3-9). There appears to be a similarity between K and $S_{max}$ values of the soils, one that reflects the Al content of the soils. Mean K values of 6.9, 8.6, and 20.9 mmol P $kg^{-1}$ were obtained for low-, medium-, and high-Al soils, respectively. These values were comparable to those obtained by Zhou (1994) for eight spodic samples from Florida. His values ranged from 2.5 to 19.8 mmol P $kg^{-1}$ with a mean of 14.6 mmol P $kg^{-1}$.

The Freundlich exponent, n did not vary much. This parameter which has been used synonymously to Langmuir constant b, was found closely related to exchangeable Al in acid soils and exchangeable Ca in neutral and calcareous soils (Fitter and Sutton, 1975).

Table 3-9. Phosphorus sorption parameters for the spodic horizons obtained from the linear Freundlich equation. K is adsorption coefficient; n is a constant.

| Soil | Aerobic | | Anaerobic | |
|---|---|---|---|---|
| | K mmol P $kg^{-1}$ | n L $kg^{-1}$ | K mmol P $kg^{-1}$ | n L $kg^{-1}$ |
| I. Low-Al | | | | |
| EauGallie | 11.76 | 0.51 | 9.79 | 0.51 |
| Immokalee | 7.06 | 0.53 | 6.15 | 0.52 |
| Pomello | 8.07 | 0.40 | 8.77 | 0.40 |
| Vero | 4.05 | 0.47 | 4.55 | 0.55 |
| Wabasso | 3.50 | 0.45 | 4.38 | 0.47 |
| | **6.89**[§] | **0.47** | **6.73** | **0.49** |
| II. Medium-Al | | | | |
| Cornelia | 5.91 | 0.50 | 7.45 | 0.46 |
| Leon | 13.55 | 0.31 | 19.35 | 0.42 |
| Myakka | 7.99 | 0.56 | 8.22 | 0.61 |
| Narcoose | 4.57 | 0.47 | 4.06 | 0.35 |
| Oldsmar | 9.85 | 0.54 | 13.15 | 0.55 |
| Sapelo | 9.56 | 0.34 | 10.17 | 0.40 |
| | **8.57** | **0.45** | **10.40** | **0.46** |
| III. High-Al | | | | |
| Kingsferry | 5.47 | 0.42 | 8.36 | 0.44 |
| Ona | 8.52 | 0.54 | 8.64 | 0.22 |
| Pomona | 24.09 | 0.45 | 48.86 | 0.60 |
| Smyrna | 18.35 | 0.52 | 18.42 | 0.51 |
| Wauchula | 47.84 | 0.57 | 47.78 | 0.58 |
| | **20.85** | **0.50** | **26.41** | **0.47** |

[§] Mean values.

Bache and Williams (1971) proposed a sorption index (SI), dS/dlog C, obtained from the slope of a Temkin plot of S versus log C. Comparison of these values with other sorption indices such as $S_{max}$ and K gave similarities that concur with the Al content of the soils. Mean SI values of 1.59, 3.02, and 4.26 were obtained for low-, medium-, and high-Al soils, respectively (Table 3-10).

Similar to Langmuir $S_{max}$, the adsorption maxima obtained from the quadratic equation represent the adsorption capacities of the soils. Thus, it was not surprising that these values were in excellent agreement with those obtained from the Langmuir equation. Mean $S_{max}$ values calculated from the quadratic equation were 7.50, 11.61, and 16.85 mmol P $kg^{-1}$ for low-, medium-, and high-Al soils, respectively (Table 3-11). The corresponding Langmuir $S_{max}$ values for these soils were 7.55, 11.08, and 17.49 mmol P $kg^{-1}$.

Phosphorus Desorption Behavior

The desorbability of P in the spodic horizons appeared to be a function of their Al content. Regardless of the amount initially adsorbed, desorption of P was highest for low-Al soils (Fig. 3-8). Desorption patterns were similar for medium-Al soils except for Leon, a soil with high P buffer capacity. Almost 50% of the initially adsorbed P was released into solution during the first extraction. Desorption of P in these soils was almost complete after nine successive 24-h extractions (Table 3-12). The high-Al soils retained a high proportion of the P adsorbed, except for Ona which behaved more like a low P-sorbing soil. Not including Ona, these soils released just over 25 % of the P initially adsorbed (Table 3-12). The high desorbability of P in Ona is directly related to

Table 3-10. Sorption index for the spodic horizons obtained from Temkin plot of S versus log C.

| Soil | Aerobic | Anaerobic |
|---|---|---|
| | -------L $kg^{-1}$------ | |
| I. Low-Al | | |
| EauGallie | 2.48 | 2.04 |
| Immokalee | 1.55 | 0.91 |
| Pomello | 2.19 | 1.65 |
| Vero | 0.86 | 0.70 |
| Wabasso | 0.85 | 0.59 |
| | **1.59**[§] | **1.18** |
| II. Medium-Al | | |
| Cornelia | 3.05 | 3.82 |
| Leon | 3.50 | 4.15 |
| Myakka | 2.53 | 1.94 |
| Narcoose | 2.76 | 1.64 |
| Oldsmar | 3.15 | 3.21 |
| Sapelo | 3.15 | 1.84 |
| | **3.02** | **2.77** |
| III. High-Al | | |
| Kingsferry | 1.16 | 1.20 |
| Ona | 5.33 | 3.40 |
| Pomona | 5.02 | 7.33 |
| Smyrna | 3.55 | 3.50 |
| Wauchula | 6.25 | 6.32 |
| | **4.30** | **4.40** |

[§] Mean values.

Table 3-11. Phosphorus sorption maximum for the spodic horizons obtained from the Quadratic equation.

| Soil | Aerobic | Anaerobic |
|---|---|---|
| | ------mmol P $kg^{-1}$------ | |
| I. Low-Al | | |
| EauGallie | 10.35 | 9.42 |
| Immokalee | 7.24 | 4.46 |
| Pomello | 11.87 | 7.79 |
| Vero | 4.12 | 2.07 |
| Wabasso | 3.93 | 2.20 |
| | **7.50**[§] | **5.19** |
| II. Medium-Al | | |
| Cornelia | 8.23 | 10.64 |
| Leon | 18.33 | 19.64 |
| Myakka | 8.30 | 5.92 |
| Narcoose | 8.43 | 3.99 |
| Oldsmar | 12.98 | 10.68 |
| Sapelo | 13.42 | 9.30 |
| | **11.61** | **10.03** |
| III. High-Al | | |
| Kingsferry | 5.68 | 6.91 |
| Ona | 10.78 | 9.31 |
| Pomona | 19.97 | 31.95 |
| Smyrna | 14.53 | 16.19 |
| Wauchula | 33.30 | 34.58 |
| | **16.85** | **19.79** |

[§] Mean values.

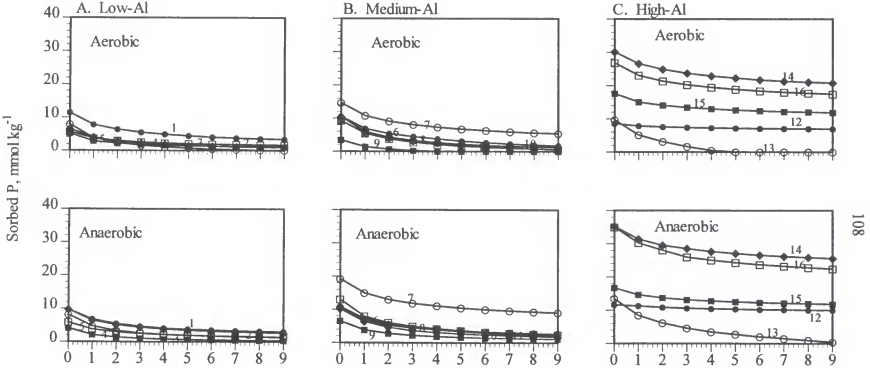



Fig. 3-8. The amount of P remaining following sequential desorption in 0.01M KCl for low-, medium-, and high-Al soils under aerobic and anaerobic conditions. 1-EauGallie; 2-Immokalee; 3-Pomello; 4-Vero; 5-Wabasso; 6-Cornelia; 7-Leon; 8-Myakka; 9-Narcoose; 10-Oldsmar; 11-Sapelo; 12-Kingsferry; 13-Ona; 14-Pomona; 15-Smyrna; 16-Wauchula.

Table 3-12. Desorbability of phosphorus in the spodic horizons under aerobic and anaerobic conditions. Values are P desorbed expressed as percent of added P sorbed.

| Soil | Aerobic | Anaerobic |
|---|---|---|
| I. Low-Al | | |
| EauGallie | 70.45 | 68.35 |
| Immokalee | 98.87 | 83.82 |
| Pomello | 85.33 | 72.56 |
| Vero | 78.05 | 90.58 |
| Wabasso | 70.18 | 74.56 |
| | **80.58**[§] | **77.97** |
| II. Medium-Al | | |
| Cornelia | 83.87 | 80.77 |
| Leon | 63.26 | 52.94 |
| Myakka | 88.01 | 82.67 |
| Narcoose | 98.26 | 83.38 |
| Oldsmar | 93.49 | 80.68 |
| Sapelo | 86.61 | 75.26 |
| | **85.58** | **75.95** |
| III. High-Al | | |
| Kingsferry | 19.16 | 14.10 |
| Ona | 98.97 | 97.15 |
| Pomona | 30.96 | 27.41 |
| Smyrna | 32.43 | 29.51 |
| Wauchula | 34.89 | 35.88 |
| | **43.28** | **40.81** |

[§] Mean values.

its high native P content. The desorption of P is greatly influenced by the extent of saturation of the sorption complex. Thus, for a P-saturated soil like Ona, the greater ease of desorption at higher saturation arises from the fact that the energy of P sorption decreases with increasing surface coverage.

When the amount of P sorbed by the soils at each desorption step was expressed as a percentage of P initially adsorbed, and all starting values for adsorbed P were set at 100%, the soils exhibited varying degrees of hysteresis (Fig. 3-9). The observed irreversibility was most pronounced in high-Al soils, where over 70% of the added P remained in the adsorbed phase after nine desorptions. Zhou (1994) reported greater desorbability of P in untreated Bh than the Bh samples in which Al-organic matter complexes were removed. He concluded that the P sorption on metal organic complexes in Bh samples is more reversible than that on inorganic metal oxides.

The irreversibility of sorption-desorption reactions has been generally attributed to a shift in the form of P held at the surface from a more loosely bound to a more tightly bound type. The exact nature of this phase change is not well understood and several mechanisms have been proposed. These include the precipitation of discrete phosphate minerals (Chen et al., 1973; van Riemsdijk et al., 1984), the shift from a monodentate to a bidentate form of sorbed P (Hingston et al., 1974; Barrow and Shaw, 1975; Munns and Fox, 1976), and the diffusive penetration of surface-sorbed P into soil components (McLaughlin et al., 1977; Ryden et al., 1977; Barrow, 1983; Willett et al., 1988).

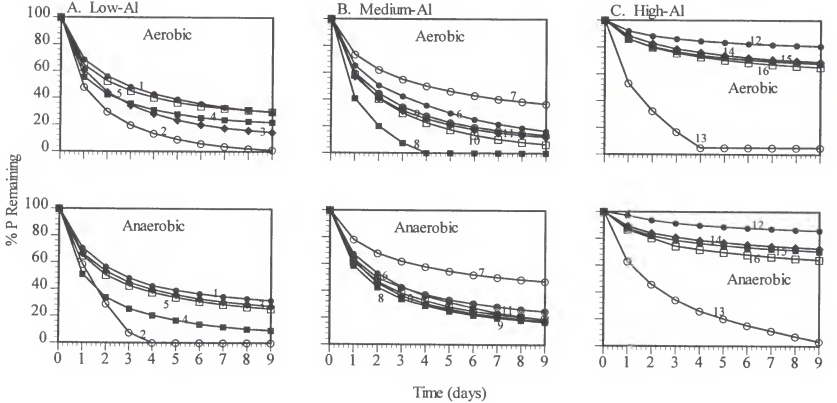



Fig. 3-9. Percent phosphorus remaining after sequential desorption in 0.01M KCl for low-Al, medium-Al and high-Al soils under aerobic and anaerobic conditions. 1-EauGallie; 2-Immokalee; 3-Pomello; 4-Vero; 5-Wabasso; 6-Cornelia; 7-Leon; 8-Myakka; 9-Narcoose; 10-Oldsmar; 11-Sapelo; 12-Kingsferry; 13-Ona; 14-Pomona; 15-Smyrna; 16-Wauchula.

Correlation of Sorption Parameters with Soil Properties

Sorption and desorption of P by soils are influenced among other factors, by the nature and amount of sorbing components, pH of the sorption system, and the saturation of the sorption complex. In acid soils, the reactivity of inorganic P is often related to the amounts of reactive Fe and Al components. It is well established in the literature, however, that the various pools of Fe and Al in soils vary appreciably in their ability to sorb P. In general, short range order (amorphous) components sorb considerably greater P than their crystalline counterparts, and crystalline hydrous metal oxides usually sorb more P than layer silicates (McLaughlin et al., 1981; Syers and Iskandar, 1981). In order to identify the Fe and Al forms along with other soil variables that were involved in the sorption and release of P by the spodic horizons, simple correlation and regression analyses were performed. There was an excellent agreement among the P sorption parameters obtained under aerobic and anaerobic conditions (Fig. 3-10), thus, it was decided to limit the discussion of the correlations to aerobic soils. Given the high positive correlations between aerobic and anaerobic parameters, prediction of P sorption by the different soil variables should be applicable to both the aerobic and anaerobic systems. Table 3-13 gives the definition of the symbols used in the correlation and regression analyses.

The P sorption maxima obtained from the Langmuir (LSmax) and quadratic (QSmax) equations, along with the Freundlich K (FK) and slope derived from the Temkin equation (TEMSI) correlated well with all the forms of Al (Table 3-14).

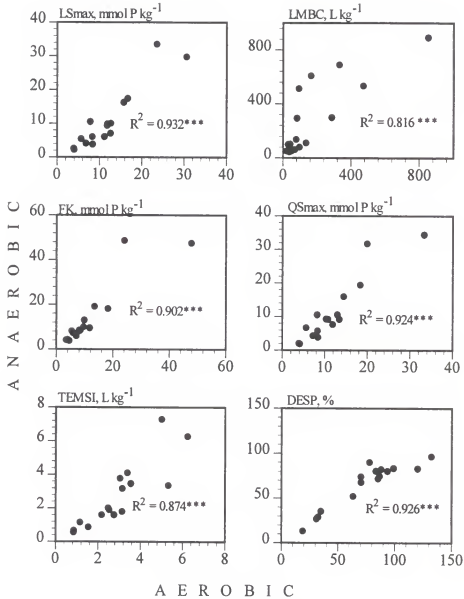



Fig. 3-10. Linear relationships between P sorption parameters obtained under aerobic and anaerobic conditions. *** Denotes significance at $p<0.001$.

Table 3-13. Definition of terms used in the correlation and regression analyses.

| Symbol | Definition |
|---|---|
| LSmax | Langmuir sorption maximum, *mmol P $kg^{-1}$ soil.* |
| LK | Langmuir bonding energy constant, *L $mmol^{-1}$ P.* |
| LMBC | Langmuir maximum buffer capacity, *L $kg^{-1}$.* |
| FK | Freundlich adsorption constant, *mmol P $kg^{-1}$.* |
| Fn | Freundlich exponent, *L $kg^{-1}$.* |
| QSmax | Sorption maximum obtained from the quadratic equation, *mmol P $kg^{-1}$ soil.* |
| TEMSI | Slope obtained fromTemkin plot of S versus log C, *L $kg^{-1}$* . Also called sorption index. |
| DESP | Readily desorbable P expressed as percentage of initially sorbed P. |
| pH | pH of soil measured in deionized water. |
| OC | Soil organic carbon, *g $kg^{-1}$ soil.* |
| CLAY | Percentage of clay in soil. |
| AL1 | Oxalate extractable Al, *mmol $kg^{-1}$ soil.* |
| FE1 | Oxalate extractable Fe, *mmol $kg^{-1}$ soil.* |
| ALFE1 | Sum of AL1 and FE1, *mmol $kg^{-1}$ soil.* |
| AL2 | CDB extractable Al, *mmol $kg^{-1}$ soil.* |
| FE2 | CDB extractable Fe, *mmol $kg^{-1}$ soil.* |
| ALFE2 | Sum of AL2 and FE2, *mmol $kg^{-1}$ soil.* |
| AL3 | Pyrophosphate extractable Al, *mmol $kg^{-1}$ soil.* |
| FE3 | Pyrophosphate extractable Fe, *mmol $kg^{-1}$ soil.* |
| ALFE3 | Sum of AL3 and FE3, *mmol $kg^{-1}$ soil.* |
| FE4 | Amount of Fe in goethite and hematite (FE2-FE1), *mmol $kg^{-1}$ soil.* |
| AL4 | Potassium chloride extractable Al, *mmol $kg^{-1}$ soil.* |
| AL5 | Cupric chloride extractable Al, *mmol $kg^{-1}$ soil.* |
| CA | Barium chloride extractable Ca, *mmol $kg^{-1}$ soil.* |
| MG | Barium chloride extractable Mg, *mmol $kg^{-1}$ soil.* |
| TOTP | Total phosphorus in soil, *mmol P $kg^{-1}$ soil.* |

Table 3-14. Correlation of P sorption parameters with selected soil variables for the spodic samples studied under aerobic conditions (n=48). ***, **, * Denote significance at $p<0.001$, $p<0.01$, and $p<0.05$, respectively.

| | LSmax | Lb | LMBC | FK | Fn | QSmax | TEMSI | DESP |
|---|---|---|---|---|---|---|---|---|
| pH | -0.205 | 0.056 | -0.050 | -0.054 | 0.138 | -0.221 | -0.211 | -0.076 |
| OC | 0.137 | -0.019 | 0.044 | 0.065 | 0.108 | 0.125 | 0.206 | -0.022 |
| CLAY | 0.260 | 0.003 | 0.056 | 0.277 | 0.053 | 0.307* | 0.373** | 0.068 |
| AL1 | 0.381** | 0.378** | 0.380** | 0.361* | -0.019 | 0.313* | 0.369** | -0.598*** |
| FE1 | -0.251 | -0.298* | -0.232 | -0.206 | 0.106 | -0.252 | -0.114 | 0.075 |
| ALFE1 | 0.357* | 0.347* | 0.368* | 0.346* | -0.005 | 0.287* | 0.363* | -0.604*** |
| AL2 | 0.484*** | 0.332* | 0.423** | 0.425** | 0.044 | 0.406** | 0.551*** | -0.446** |
| FE2 | -0.371** | -0.172 | -0.254 | -0.264 | 0.064 | -0.363* | -0.318* | 0.065 |
| ALFE2 | 0.406** | 0.301* | 0.374** | 0.374** | 0.064 | 0.327** | 0.492*** | -0.450** |
| AL3 | 0.373** | 0.380** | 0.378** | 0.366* | 0.006 | 0.302* | 0.353* | -0.619*** |
| FE3 | -0.293* | -0.245 | -0.234 | -0.222 | 0.098 | -0.304* | -0.192 | 0.027 |
| ALFE3 | 0.350* | 0.368* | 0.347* | 0.361* | 0.016 | 0.277 | 0.341* | -0.630*** |
| FE4 | -0.318* | 0.003 | -0.060 | -0.204 | 0.004 | -0.307* | -0.355* | 0.030 |
| AL4 | 0.498*** | 0.378** | 0.468*** | 0.380** | -0.026 | 0.532*** | 0.363* | -0.079 |
| AL5 | 0.781*** | 0.732*** | 0.816*** | 0.792*** | 0.121 | 0.715*** | 0.610*** | -0.730*** |
| CA | -0.392** | -0.255 | -0.314* | -0.299* | 0.104 | -0.396** | -0.209 | 0.293* |
| MG | -0.344* | -0.060 | -0.206 | -0.236 | 0.038 | -0.336* | -0.344* | 0.119 |
| TOTP | -0.073 | -0.471*** | -0.246 | -0.141 | 0.260 | -0.105 | 0.390** | 0.438** |

Correlation was highest consistently for $CuCl_2$-extractable Al (AL5), indicating that the Al associated with organic matter is the major sorbent of P in the spodic horizons studied. Similarly, organically bound Al extracted by pyrophosphate reagent (AL3) gave significant correlation with the P sorption indices. Correlation coefficients however, were lower compared to those obtained for $CuCl_2$-Al. The difference could have resulted from the mode of action of the $CuCl_2$ reagent. While the precise mechanism of soil-pyrophosphate reaction is still uncertain (Parfitt and Childs, 1988), it is well established that the $CuCl_2$ reagent, in addition to organic matter-complexed Al, extracts some inorganic Al forms. The reactive Al pool extractable with $CuCl_2$ includes readily exchangeable $Al^{3+}$, positively charged hydroxy-Al polymers, and interlayered hydroxy-Al in vermicullite and montmorillonite. It also includes the $Al^{3+}$ ions and hydroxy-Al associated with soil organic matter in the forms of non-exchangeable organo-Al complex, and the more soluble forms of metastable, amorphous $Al(OH)_3$ (Juo and Kamprath, 1979).

The sorption of P by Al-organic matter complexes in acid soils has been successfully demonstrated by Haynes and Swift (1989). They reported P sorption by Al-organic matter that increased with pH and drying of the soils. They attributed the increased P sorption by Al-organic matter complexes with pH to enhanced hydrolysis and polymerization of hydroxy-Al associated with the organic matter. The positive effect of drying on P sorption was related to the condensation of organic matter which results in increased accessibility of phosphate to adsorption sites on the hydroxy-Al. For the spodic

horizons that undergo flooding and drying cycles, the latter could be a possible mechanism by which sorption capacities of these soils could be enhanced.

The positive correlations of P sorption with other forms of Al i.e., oxalate-Al (AL1), CDB-Al (AL2), and KCl-Al (AL4) were further proof that regardless of the extractant used, Al was the dominant factor in P retention by the Bh samples. Acid oxalate reagent is known to dissolve short-range order components. This form of Fe and Al correlated positively with P sorption in tropical and subtropical soils (Loganathan et al., 1987), Canadian Spodosols (Yuan and Lavkulich, 1994), Bh samples from south Florida (Nair et al., 1997), and German soils (Freese et al., 1992), among others. KCl-extractable Al (AL4) had as good a correlation with P retention as AL1, AL3, and AL2. Relative to the other forms of Fe and Al, the contribution of CDB-extractable Fe and Al to P sorption was expected to be small. Ryden and Pratt (1980) reported that crystalline Fe and Al hydrous oxides sorb 10-100 times less P than their amorphous counterparts. The rather high correlation of CDB-Al with P sorption in the Bh samples studied is due to the fact that CDB extracts both the amorphous and crystalline Fe and Al hydr(oxides) (Boero and Schwertmann, 1989; Skjemstad et al., 1989). The difference between CDB and oxalate-extractable Fe ($Fe_d$-$Fe_o$) represents the amount of Fe in goethite and hematite (Parfitt and Childs, 1988). This fraction of Fe along with the other forms gave significant negative correlations with the P sorption parameters. This is somewhat surprising considering that both metals were expected to exhibit a synergistic effect on P sorption. However, when the two extremely high levels of Fe being that of Cornelia and Vero soils (Table 3-3) were excluded from the analysis, correlation coefficients remained negative,

but were much smaller and insignificant. Apparently, the relationship between P sorption and Fe in those two soils were forcing the correlation to yield a spurious value. In general, extractable Fe levels were low and would not be expected to contribute significantly to P sorption by the spodic horizons. These findings agree with those of Zhou (1994) who reported significant correlations between P sorption capacity of Bh samples and all forms of Al but not Fe. Agbenin and Tiessen (1994) observed a more dominant role of Al than Fe in Brazilian soils that are dominated by amorphous and crystalline forms of Fe.

Organic carbon did not show significant correlation with any of the P sorption parameters; however, its high correlation with the organically bound Al (AL3) ($r=0.505$, $p<0.001$), implies active participation of organic matter in P sorption. The role of organic matter in augmenting P sorption in acid soils has often been attributed to the association of the soil organic matter with Fe and Al hydroxides, which provide an active surface for P sorption (Sanyal and De Datta, 1991).

There was a positive correlation of QSmax ($r=0.307$, $p<0.05$) and TEMSI ($r=0.373$, $p<0.01$) with the clay content of the soils. A significant correlation between clay content and P sorption parameters has been reported by several workers (Loganathan et al., 1987; Owusu-Bennoah and Acquaye, 1989; Solis and Torrent, 1989; Wada et al., 1989; Sanyal and De Datta, 1993), one that is considered as a mere reflection of the effect of specific surface area on P retention. Hydrous oxides of Fe and Al occur as fine coatings on surfaces of clay minerals in soil (Haynes, 1983). These coatings have large surface areas that can hold a significant amount of P, thereby implying a secondary role of

clays in P sorption (Ryden and Pratt, 1980). The negative correlations between P sorption and exchangeable bases (CA and MG) were to be expected in acid mineral soils dominated by Al and Fe.

The binding energy constant b (Lb) and the maximum buffer capacity (LMBC) gave high positive correlations with the different forms of Al but not with any of the Fe forms (Table 3-14). This suggests that P is sorbed more tightly on Al surfaces than it is on Fe surfaces. There was a negative correlation between Lb and the amount of native P (TOTP) in the soils ($r=-0.471$, $p<0.001$). This was expected as the energy of P sorption decreases with increasing surface coverage. No correlation was found between Freundlich constant, n (Fn) and the soil properties. This can be attributed to the lack of variability in the values necessary to yield some type of correlation. Fitter and Sutton (1975) found a significant correlation of n with exchangeable Al in acid soils and with exchangeable Ca in calcareous soils.

The amount of sequentially desorbed P (DESP) was negatively correlated with all the forms of Al, indicating lower desorbability of P in the Bh samples high in Al. The positive correlation of DESP with exchangeable Ca ($r=0.293$, $p<0.05$) and native P ($r=0.438$, $p<0.01$) suggests that in the presence of more Ca and native P, greater release of freshly added P was to be expected in these soils.

Prediction of P Sorption by Soil Properties

The soil components involved in P sorption are themselves interrelated, thus it is difficult to determine which components make the largest contribution to P sorption based on simple correlation alone. To examine the relative contributions of the soil

properties to P sorption by the soils a stepwise model-building procedure known as the maximum $R^2$ improvement technique (MAXR) was used (SAS, 1985). The MAXR method begins by finding the one-variable model which produces the highest $R^2$. Then another variable, the one that yields the greatest improvement in $R^2$, is added. Once the two-variable model is obtained, the variables in the model are compared to the other variables to determine if removing one variable and replacing it with the other variable would increase $R^2$. The variables producing the highest $R^2$ are kept, and the procedure is repeated until no further significant improvement in $R^2$ is obtained. For brevity, only results for the best three-variable models are presented.

Consistent with the results obtained from the correlation analyses, $CuCl_2$-Al (AL5) accounted for most of the variation in all P sorption parameters (Table 3-15). The combination of AL5, AL3, and AL2 explained about 80% of the variability in P sorption, 61% of which came from AL5 alone. The contribution of AL2 was small but significant. Holding AL5 and AL3 constant, the model predicted AL2 to increase LSmax by a factor of 0.07 for every unit of AL2 added. The presence of AL3, however, was predicted to have a small negative effect on LSmax. This was regarded not as a negative effect per se, but rather as a consequence of having two variables with overlapping properties in the model. As alluded to earlier, AL5 and AL3 were taken to represent organically bound Al, with both variables showing significant relationship with LSmax. However, based on the simple correlation, LSmax correlated much more strongly with AL5 ($r=0.781$, $p<0.001$) than with AL3 ($r=0.373$, $p<0.01$). The small negative estimate for AL3 could very well

Table 3-15. Stepwise regression results for the relationships between P sorption parameters and selected soil variables. Only the best three-variable models based on the $R^2$ values are presented.

| Dependent Variable | Independent Variable | Parameter Estimate | Standard Error | Type I F | *p*-value | Partial $R^2$ |
|---|---|---|---|---|---|---|
| LSmax | Intercept | 5.30 | 0.84 | 39.34 | 0.0001 | |
| | AL5 | 0.19 | 0.02 | 93.39 | 0.0001 | 0.610 |
| | AL2 | 0.07 | 0.02 | 14.64 | 0.0004 | 0.090 |
| | AL3 | -0.09 | 0.02 | 28.93 | 0.0001 | 0.075 |
| Lb | Intercept | 7.50 | 1.05 | 51.18 | 0.0001 | |
| | AL5 | 0.13 | 0.02 | 73.40 | 0.0001 | 0.535 |
| | CA | 0.26 | 0.12 | 4.47 | 0.0400 | 0.146 |
| | TOTP | -0.18 | 0.03 | 26.59 | 0.0010 | 0.030 |
| LMBC | Intercept | -52.30 | 36.79 | 2.02 | 0.1623 | |
| | AL5 | 6.38 | 0.58 | 122.08 | 0.0001 | 0.666 |
| | AL3 | -0.98 | 0.23 | 18.10 | 0.0001 | 0.111 |
| | CLAY | 14.56 | 6.94 | 4.40 | 0.0417 | 0.020 |
| Lb | Intercept | -0.06 | 1.99 | 0.00 | 0.9740 | |
| | AL5 | 0.31 | 0.03 | 96.42 | 0.0001 | 0.628 |
| | AL3 | -0.05 | 0.01 | 13.76 | 0.0006 | 0.104 |
| | CLAY | 0.89 | 0.38 | 5.54 | 0.0231 | 0.030 |
| Lb | Intercept | 0.450 | 0.020 | 752.83 | 0.0001 | |
| | AL5 | 0.001 | 0.001 | 7.48 | 0.0090 | 0.068 |
| | AL2 | -0.001 | 0.000 | 6.30 | 0.0160 | 0.024 |
| | TOTP | 0.002 | 0.001 | 10.00 | 0.0020 | 0.113 |
| QSmax | Intercept | 5.87 | 1.03 | 32.64 | 0.0001 | |
| | AL5 | 0.19 | 0.02 | 63.49 | 0.0001 | 0.511 |
| | AL2 | 0.07 | 0.02 | 8.22 | 0.0063 | 0.112 |
| | AL3 | -0.09 | 0.02 | 19.40 | 0.0001 | 0.060 |
| TEMSI | Intercept | 0.63 | 0.080 | 55.55 | 0.0001 | |
| | AL5 | 0.02 | 0.002 | 82.60 | 0.0001 | 0.372 |
| | AL3 | -0.004 | 0.001 | 23.05 | 0.0001 | 0.222 |
| | TOTP | 0.024 | 0.003 | 56.44 | 0.0001 | 0.140 |
| DESP | Intercept | 92.77 | 4.02 | 532.17 | 0.0001 | |
| | AL5 | -0.26 | 0.10 | 6.59 | 0.0137 | 0.533 |
| | AL3 | -0.16 | 0.04 | 14.25 | 0.0005 | 0.121 |
| | TOTP | 0.86 | 0.15 | 32.21 | 0.0001 | 0.085 |

be due to the overwhelming effect of AL5 on LSmax which apparently was masking the effect of AL3.

The same three variables appeared in the model predicting QSmax. This was expected as LSmax and QSmax which both represent the maximum P sorption capacity of the soils were almost in a 1:1 relationship. The combined effect of AL5, AL3, and AL2 accounted for about 70% of the variability in QSmax, with AL5 contributing over 50%.

The Langmuir binding constant (Lb) was best predicted by AL5, CA, and the CLAY content of the soils, explaining about 80% of the variability in Lb. According to the model, AL5, and CA would increase Lb by a factor of 0.13 and 0.26 for every unit of AL5 and CA, respectively. As expected, the energy of sorption was predicted to decrease with the amount of initially sorbed P.

As was the case for LSmax, AL5 accounted for most of the variability in LMBC, FK, and TEMSI, contributing 67, 63, and 37%, respectively. Again, the negative effect of having AL3 with AL5 in the model is manifested here. The addition of CLAY in the model increased the $R^2$ value by 2 and 3%, for LMBC and FK, respectively.

About 74% of the variability in the amount of sequentially desorbed P was accounted for by the combination of AL5, AL3, and TOTP. Consistent with the correlation of DESP with AL5 and AL3, both variables were predicted to decrease release of P by these soils. The desorbability of freshly added P was expected to increase with the amount of P initially present in the soils. This is consistent with the theory that the more saturated the sorption complex is, the lower the energy of sorption becomes.

## Summary and Conclusions

The spodic samples studied exhibited P sorption capacities that were consistent with their total Al content. Mean $S_{max}$ values of 7.55, 11.08, and 17.49 mmol P $kg^{-1}$ were obtained for low-, medium-, and high-Al soils, respectively. Assuming an average thickness of 15 cm and a bulk density of 1.33 Mg $m^{-3}$, these values correspondingly would translate into maximum sorption capacities of 468, 680, and 1084 kg P $ha^{-1}$. These values were typical for Florida Bh samples (Zhou, 1994; Nair et al., 1996) but were much lower for average sorption capacity of over 3000 kg P $ha^{-1}$ estimated for Bh samples from Canada and northeastern U.S. (Laverdiere, 1982; Yuan and Lavkulich, 1994).

The ability of the soils to sorb P was influenced by flooding. The effect, however, was generally small and inconsistent. For example, flooding reduced P sorption by low- and medium-Al soils and slightly increased that of high-Al soils. The reduction in P sorption by low- and medium-Al soils upon flooding may have resulted from the hydrolysis of Fe/Al-phosphates caused by Fe reduction. The mean Al:Fe ratio in these soils was 2:1 compared to 31:1 for high-Al soils, indicating that Fe may have a played a greater role in low-Al soils. The increase in P sorption by high-Al soils was attributed to greater sorption of P by aluminum-organic matter complexes and to the formation of amorphous Al-hydroxy-phosphates. Haynes and Swift (1989) reported sorption of P by Al-organic matter complexes that increased with pH.

The soils exhibited a hysteretic P sorption-desorption behavior that was consistent with their Al content. Low-Al soils released freshly sorbed P much faster than high-Al

soils did. The high degree of hysteresis observed in high-Al soils was thought to involve some type of chemical shift in the form of sorbed P that rendered it highly irreversible.

Phosphorus sorption-desorption reactions in the spodic horizon were influenced largely by Al. Correlation and regression analyses show that $CuCl_2$-extractable Al was the single most important chemical property contributing to P retention in these soils, accounting for over 60% of the variation in P sorption. This suggests that sorption and release of P by the spodic horizon to a large extent involve Al-organic matter complexes.

# CHAPTER 4
# THE RATE AND EXTENT OF PHOSPHORUS SORPTION-DESORPTION REACTIONS IN THE SPODIC HORIZON AS INFLUENCED BY pH

## Introduction

The chemistry of phosphorus in the spodic horizon has drawn interest from environmental scientists in Florida, in large part due to the growing public concern over water quality problems associated with its lakes and streams. Low pH and high amounts of amorphous mixtures of organic matter, Al and Fe, make the spodic horizon a potentially effective sink for P. In a leaching study conducted on a typical Spodosol from a dairy farm in the Lake Okeechobee watershed, Villapando and Graetz (1992) reported substantial movement of P into the spodic horizon from the manure-impacted surface layer, under flooded and drained conditions. Phosphorus that accumulated in the spodic horizon was found largely in association with Fe and Al. More recently, Nair et al. (1995) evaluated the forms of phosphorus in the soil profiles from dairies of south Florida. They found elevated levels of Al/Fe-bound P in the spodic horizon for all dairy components, with values ranging from 46% of total P for the native areas to 78% of the total P for the intensive areas of the active dairies. Spodic horizons are naturally acidic and as such, are expected to sorb P. However, changes in pH brought about by flooding or migration of basic materials from the surface layer into the spodic horizon could alter its P sorption properties. The observed increases in exchangeable bases and soil pH, that

accompanied increased P retention by the spodic horizon in areas heavily impacted with animal wastes, prompted us to investigate the effect of pH on P sorption and release properties of these soils. An understanding of the P sorption-desorption reactions in soils as influenced by pH should help us better define the role of the spodic horizon in the transport of P in Florida Spodosols.

The capacity of a soil to sorb P has been reported to decrease with an increase in pH. Working with gibbsite and goethite, Hingston et al. (1972) observed decreased P sorption by these materials with pH. Parfitt (1977) also obtained a five fold reduction in the sorption maximum of an Oxisol when the pH was increased from 5 to 8. Increasing the pH of a New Zealand soil from 5.5 to 6.5 by liming, decreased the sorption maximum of the soil by 20% (Ryden et al., 1977). Barrow (1984) explained the reduction in P sorption in terms of the effect of pH on the charge and the electrostatic potential of the variable charge surfaces that retain P in the soil. It is well established that the main components responsible for P sorption in acid soils are Fe and Al oxides. In pure form, these oxides have a point of zero charge of about 8 and are therefore positively charged in the normal pH range of soils. With an increase in pH, the charge on these materials and their electrostatic potentials decrease. This would make reaction with the negatively charged phosphate ions more difficult, thereby reducing sorption. The increase in soil pH could also lead to an increase in microbial activity and an increased production of organic anions that could compete with P for sorption sites in the soil (Earl et al., 1979; Haynes, 1982). Syers and Sumner (1979) suggested that the initial pH and the amount of

exchangeable Al that can be precipitated by lime addition largely determine the effect of pH on P sorption by acid soils.

An opposite effect of pH on P sorption by soils has also been observed. Haynes and Swift (1989) reported sorption of P by Al-organic matter complexes that increased with pH. The authors ascribed this to increased hydrolysis and polymerization of hydroxy-Al associated with organic matter. Similarly, Bloom (1981) attributed the large sorption of P by Al-peat at high pH to the formation of Al-peat-phosphate complexes and to the precipitation of amorphous Al-hydroxy-phosphate, likely $AlH_2PO_4(OH)_2$. Mokwunye (1975) reported a similar effect of pH on P retention in Nigerian soils. He suggested that the observed increase in P adsorption was due to the increased activity of the amorphous hydroxy-Al species which adsorbed P through the surface-exchange of a hydroxyl group. Naidu et al. (1990) attributed the increased P sorption at pH values >6.0 to the formation of insoluble Ca compounds. Smillie et al. (1987) and Haynes (1984) also suggested a chemical association between sorbed P and Ca in soils, having adequate exchangeable Ca, as an important P retention mechanism.

The effect of pH on P sorption has been reported to vary with the supporting electrolyte used in P sorption studies. Barrow (1984) and Parfitt (1977) observed a decrease in sorption with pH when measurement was made in dilute solutions of NaCl or KCl, but when dilute $CaCl_2$ solution was used, P sorption by a limed soil increased (Amarasiri and Olsen, 1973; Barrow, 1984; Naidu et al., 1990). According to Barrow et al. (1980) at low pH, when the phosphated surface is positively charged, a decrease in ionic strength would make the electrostatic potential in the plane of adsorption more

positive and thus, increase retention of P. At high pH, with a phosphated surface that is negatively charged, a decrease in the ionic strength would make the potential more negative resulting in reduced sorption of P. Similar differences occur when a solution of monovalent salt such as NaCl is compared with a divalent cation such as $CaCl_2$. As a result, retention from NaCl is higher at low pH and lower at high pH.

The effect of pH on P sorption would also depend on the amount of desorbable P in the soil (Barrow, 1984). For a soil with virtually no desorbable P, the only effect of pH would be the effect on the ability of the soil to retain newly added P. But for a soil that contains some desorbable P, there could be a separate and different effect of altering pH on the desorption of P.

Transport of P with water in soils is largely dependent upon the rate and extent of P removal by soil components. In acid soils, the reaction between P and the abiotic components of soils involves the active surface Fe and Al atoms (Parfitt, 1989). The reaction of P with Fe and Al is rapid at first. It then becomes slow, and continues for a long time without reaching any true equilibrium (McLauglin et al., 1977; Barrow, 1983; Bolan et al., 1985; Parfitt, 1989). Working with synthetic oxides and hydroxides of Fe and Al, Parfitt (1978, 1989) showed that the initial adsorption reaction of phosphate is by ligand exchange with surface OH groups which are singly coordinated to Fe and Al atoms, i.e., Al-OH and Fe-OH groups. The result of this exchange reaction is the formation of an inner-sphere surface complex (Sposito, 1981) between an *o*-phosphate group and a metal which was bound to the hydroxyl group. These complexes are quite stable, showing mainly covalent or ionic bonding character. Formation of such

complexes provides a mechanism for what is referred to as specific adsorption (Sposito, 1984). The mechanism of specific phosphate adsorption by hydroxylated mineral surfaces is generally well-established. Goldberg and Sposito (1985) wrote a comprehensive review of the studies presented in support of this mechanism. Evidence pointing to the ligand exchange mechanism include kinetics of adsorption and desorption, hydroxyl ion release, infrared spectroscopy, and stereochemical calculations.

The mechanism of slow P sorption that continues long after the initial rapid sorption is not as clear. Two of the proposed mechanisms for slow P sorption in soils are solid-state diffusion (Barrow, 1983; van Riemsdijk et al., 1984) and diffusion through micropores (Barrow, 1987). Solid-state diffusion was envisaged to occur via exchange and vacancy mechanisms (Manning, 1968). In the exchange mechanism, two atoms change position whereas in the vacancy mechanism, the $HPO_4^{2-}$ or $H_2PO_4^-$ diffuses into vacant sites in crystal lattices of the sorbing matrix (Barrow, 1985). Using the diffusion model of Barrow (1983), Bolan et al. (1985) suggested that the increase in P sorption with time by Fe and Al hydroxides was caused by a redistribution of adsorbed P to the interior of the adsorbing particles by a solid-state diffusion process. Ryden et al. (1977) suggested a similar mechanism for the continued removal of P from solution by ferric hydrous oxide gel. Parfitt (1989), however, demonstrated that for a highly crystalline goethite with virtually no slow reaction, solid-state diffusion of phosphate would not readily occur. Evidence for diffusion of P into micropores was provided by Cabrera et al. (1981), who reported that the reaction of P with lepidocrocite continued for a longer period than with goethite. They pointed out that the small crystals of lepidocrocite tend

to form large aggregates with micropores between them. Diffusion of P into these micropores was probably responsible for the slow reaction. According to Parfitt (1989), the extent of P sorption during the slow penetration reactions depends on the degree of crystallinity or porosity of Fe and Al oxides.

Phosphorus sorption has been described as irreversible (Olsen and Khasawneh, 1980), that is, P sorption and desorption curves often do not coincide (Barrow, 1983). The observed irreversibility has been attributed to the unequal forward and backward sorption kinetic rates (Lindstrom et al., 1977), more specifically to the incomplete attainment of equilibrium during the slower phase of adsorption (Okajima et al., 1983; Barrow, 1983, 1985). The diffusive migration of adsorbed P inside the adsorbing surface, and/or precipitation on the surface, followed by occlusion has also been cited as a probable cause of irreversibility of P sorption (Barrow, 1983; van Riemsdijk et al., 1984; Bolan et al., 1985). The shift from monodentate to bidentate forms of sorbed P with continuing sorption reaction has also been mentioned ( Hingston et al., 1974; Bar-Yosef and Kafkaki, 1978). However, the recent work of Parfitt (1989) involving different Fe oxides demonstrated that the formation of a binuclear bridging complex between a phosphate group and two surface Fe atoms takes place at a rapid rate. Therefore, the formation of the binuclear complex is not the mechanism of the slow reaction by which P becomes less available with time (Barrow, 1987). The extent of irreversibility also depends on the nature of the surface of the sorbent. Mott (1981) states that unlike non-specifically adsorbed ions, ligand-exchanged ions do not have adsorption and desorption isotherms that are identical kinetically. For ligand-exchanged ions, desorption at constant

pH is a much slower process than adsorption. Bidentate phosphate complexes are more difficult to desorb than their monodentate counterparts (Hingston et al., 1974). Recently, Zhou (1994) reported that P sorption on metal organic complexes on Bh samples is more reversible than that on inorganic metal oxides.

The time-dependence of P sorption-desorption reactions in soils has been modeled by an array of kinetic equations including first order, second order, and Elovich equations, among others. The linear forms of these equations and the basic assumptions involved in their derivation are given in Table 4-1. According to Berkheiser et al. (1980) these equations appear to describe the phenomenon of phosphate sorption rather than the mechanism of the sorption process. It is not possible to deduce the mechanism of a reaction from the rate law alone. In order to fully elucidate the reaction mechanism, other experimental methods such as spectroscopy must be employed. Nevertheless, the parameters obtained from these equations allow us to empirically calculate the importance of several variables relative to P partitioning, of which the presence of certain mineral species and their crystallinities, time and temperature seem to be most important.

As pointed out earlier, spodic horizons are generally acidic; elevated pH levels, however, were noted in areas heavily impacted with animal wastes. This study was conducted (i) to examine P sorption and desorption behavior of the spodic horizons at various pH levels, (ii) to study the rate of P sorption and release by the soils as influenced by pH, (iii) to identify the soil components responsible for P sorption in the soils and (iv) to make deductions about the mechanism of P sorption in these soils based on the information provided by Objectives i through iii. In acid soils, the reaction of P

Table 4-1. Summary of kinetic equations used for phosphate reaction with soil constituents (From Bolan et al., 1985).

| Equation[§] | Assumptions |
|---|---|
| First order kinetics<br>$\ln C = \ln C_o - kt$ | Rate of change in concentration is proportional either to the concentration in solution or to the number of empty sites. |
| Second order kinetics<br>$(1/C_o) - (1/C) = kt$ | Rate of change in concentration is proportional to both the concentration in solution and number of empty sites. |
| Diffusion equation<br>$X = R\sqrt{t} + b$ | Rate limiting step is the diffusion of phosphate ions from the solution to the surface or from the surface to the interior of the particle. |
| Modified Langmuir<br>$X = b_i + \Delta b_i + b_{11}C/1+K_{11}C + b_{111}K_{111}C/1+K_{111}C$ | Rate of adsorption is proportional to the concentration in the solution and the number of sites; with time, adsorbed phosphate redistribution in region 1. |
| Modified Freundlich<br>$X = Kc^{b}t^{b1}$ | Phosphate reaction in soil system contained three compartments, A, B and C and reacts according to A⇌B⇌C; rate limiting step is B⁻C. |
| Elovich equation<br>$X = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t$ | Activation energy of adsorption increases linearly with surface coverage |

[§] where X is the amount of P sorbed, $C_o$ and C are the initial and the final concentration of phosphate in solution, t is time and all others are parameters.

with Fe and Al largely control the concentration of P in solution. Thus, it was hypothesized that the rate and extent of sorption and release of P by the spodic horizons will be a function of the size of the reactive Fe and Al pools in the soil relative to soil pH.

## Materials and Methods

### Soil Description

Soil samples from the spodic horizon of two Florida Spodosols namely, EauGallie (sandy, siliceous, hyperthermic Alfic Arenic Alaquods) and Wauchula (sandy, siliceous, hyperthermic Ultic Alaquods) fine sands were used in the study. These soils were chosen based on their total Al and Fe contents. Wauchula represents the soils dominated by Al while EauGallie represents the soils low in both Al and Fe.

### Soil pH Adjustment

Titration curves were prepared to determine the amount of acid or base required to adjust the pH of the soils to specific values (Appendix B). Ten-gram samples of soil were equilibrated with 100 mL of 0.01M KCl for 24 hours. Titration was carried out with 0.1M HCl on the acid side and with 0.1M KOH on the alkaline side of the native pH of the soils. The pH levels used were 3.5, ambient, 5.0, and 6.0. Natural pH values at 0.01M KCl were 3.9 and 4.1 for EauGallie and Wauchula, respectively. Soil pH adjustment was made by suspending 200-g samples in 200 mL of 0.01M KCl solution. The amount of acid or base extrapolated from the titration curves was then added and the pH monitored daily. Once the desired pH of the suspension was attained, the soils were air-dried, passed through a 2-mm sieve, and stored in plastic bags until ready for use.

Chemical and Mineralogical Analyses

Initial soils. Soil reaction (pH) was measured in water and 1M KCl using a 1:1 soil:solution ratio (McLean, 1982). Organic C was estimated by rapid oxidation with a hot mixture of $K_2Cr_2O_7$ and $H_2SO_4$ (Nelson and Sommers, 1982). Exchangeable Ca, Mg, K, and Na were extracted from a 0.1M $BaCl_2$ solution following a 2-h equilibration (Gillman, 1979). Exchangeable Al was determined by extraction with 1M KCl (Barnhisel and Bertsch, 1982). The sum of exchangeable cations and Al was taken to represent the effective cation exchange capacity (ECEC) of the soil (Juo et al., 1976). The elemental concentrations of Al, Fe, and P were determined by digesting a finely ground sample in nitric-perchloric acid mixture (Olsen and Sommers, 1982). The analysis of Al, Fe, and P in the digestate was done by Inductively Coupled Argon Plasma (ICAP) emission spectrophotometry.

The mineralogy of the soils was determined using clay mounts on ceramic tiles, saturated with Mg or K, and washed free of salts. X-ray diffraction (XRD) analysis was performed using a computer-controlled XRD system. The mounts were scanned at $2^0$ $2\theta$ per minute with CuK$\alpha$ radiation at 35 kV and 20 mA.

All soils. The forms and distribution of Fe and Al in the Bh horizons at various pH levels were determined by selective dissolution. Reactive Al was estimated by extraction with 1M $CuCl_2 \cdot H_2O$ (Juo and Kamprath, 1979). Aluminum and Fe associated with organic matter were extracted with 0.01M $Na_4P_2O_7$ (Wada and Higashi, 1976). Amorphous and crystalline forms of Al and Fe were dissolved in acidified 0.2M $(NH_4)_2C_2O_4$ (McKeague and Day, 1966), and citrate-dithionite-bicarbonate (Mehra and

Jackson, 1960), respectively. Exchangeable Al was determined using 1M KCl extraction (Barnhisel and Bertsch, 1982). Iron and Al in the extracts were analyzed using an ICAP emission spectrophotometer.

Native and freshly added P in the soils at various pH levels were separated sequentially into loosely bound P, Fe/Al-P, and Ca-P by extraction with 1M $NH_4Cl$, 0.1M NaOH, and 0.5M HCl (Hieltjes and Lijklema, 1980). Moderately labile organic P was estimated by taking the difference between P in digested and undigested NaOH extract. Digestion was done in persulfate-sulfuric acid mixture at 380°C (APHA, 1985). All P determinations were done using the procedure of Murphy and Riley (1962) on a Technicon Auto Analyzer II.

The surface charge properties of the soils were determined by potentiometric titrations and ion adsorption measurements. These techniques were delineated in Chapter 2 of this dissertation.

Phosphorus Sorption-Desorption Studies

This study was originally designed to involve the use of reaction vessels similar to that shown in Appendix C. This setup is equipped with pH and Pt electrodes, calomel, and gas lines which allow easy control of pH and redox conditions (Patrick et al., 1973). However, preliminary work with the spodic samples used in this study showed that such system may not work for a soil that contains predominantly sand-size particles. Some of the difficulties encountered include: (i) uneven stirring of the suspension due largely to the predominance of denser particles that sat on the bottom of the flask, (ii) the substantial increase in ionic strength of the soil solution from contamination with KCl

that leaked from the pH electrode, (iii) difficulty in obtaining a representative subsample, and (iv) decomposition of the soil particles from prolonged stirring, thus increasing the surface area of the soil during the experiment. The net effect of this would be an increase of the reaction rate with time. In view of the problems presented, all sorption and desorption experiments were done using the batch incubation procedure.

Phosphorus sorption. Duplicate 1-gram samples were placed in 50-mL centrifuge tubes. The samples were suspended in 20 mL of 0.01M KCl containing P ranging from 0 to 3.223 mM P added as $KH_2PO_4$, and equilibrated in an end-over-end shaker for 24 hours at room temperature. The samples were then centrifuged at 3620 *g* for 10 min, filtered through a 0.45μm filter, and analyzed for P using the ascorbic acid method of Murphy and Riley (1962).

Phosphorus desorption. Desorbability of P in the spodic samples was studied by initially equilibrating the soils with 20 mL of 0.01M KCl solution containing 3.223 mM P as $KH_2PO_4$. After 24-h shaking, the samples were centrifuged at 3620 *g* for 10 min, filtered through a 0.45μm filter, and analyzed for P. Phosphorus lost from solution represented the starting value for adsorbed P. The "P-saturated" soils were then subjected to sequential desorption with 20 mL of 0.01M KCl equilibrated in an end-over-end shaker for 24 hours. Sequentially desorbable P was determined by summing the total P desorbed per unit mass of soil after nine 24-h successive extractions.

Model fitting. Sorption data were fitted by regression analyses to the linear form of Langmuir and Freundlich equations. The regression models used were

i) Langmuir

$$C/S = 1/bS_{max} + C/S_{max} \qquad (4\text{-}1)$$

where C is the final solution P concentration (mM P), S is the amount of added and native P sorbed (mmol P $kg^{-1}$), $S_{max}$ is the sorption maximum, and b is a constant related to binding energy (L $mmol^{-1}$ P). The product of $S_{max}$ and b represents the maximum buffer capacity (MBC) of the soil.

ii) Freundlich

$$\log S = \log K + n\log C \qquad (4\text{-}2)$$

where S and C are as previously defined, K is the adsorption coefficient (mmol P $kg^{-1}$), and n is a constant (L $kg^{-1}$).

Kinetics of Phosphorus Sorption-Desorption

Phosphorus sorption. One-gram of each soil sample was placed into 50-mL centrifuge tubes. To these soils, 20 mL of 0.01M KCl solution having different P concentrations (as $KH_2PO_4$) were added. The initial P concentrations used were such that the resulting amount of P in the soils would be equivalent to 1/2, 1, and 2 times their maximum P sorption capacities ($S_{max}$) obtained from the Langmuir equation. For EauGallie, these rates correspond to 0.30, 0.59, and 1.18 mM P. And for Wauchula, these rates are equal to 0.77, 1.53, and 3.06 mM P. The tubes were placed on a mechanical shaker for different periods from 0.01 to 72 h. At the end of each shaking period, the samples were immediately filtered using disposable syringe filters. Phosphorus in the supernatant was analyzed on a Technicon Auto Analyzer II using the ascorbic acid method of Murphy and Riley (1962).

Phosphorus desorption. The release of P by soils was studied using P-amended soils. Solution P (as $KH_2PO_4$) was added to the soils at levels equivalent to 1/2, 1, and 2 times their sorption maximum ($S_{max}$) estimated from the Langmuir equation. EauGallie soil was treated with 5.93, 11.85, and 23.70 mmol P $kg^{-1}$. The rates used for Wauchula were 15.33, 30.65, 61.30 mmol P $kg^{-1}$. The samples were incubated aerobically at room temperature for 28 days in small plastic bags at a moisture level equivalent to field capacity. The moisture content of the soils was maintained by adding appropriate amounts of deionized water twice a week. After incubation, the soils were air-dried, and sieved through a 2-mm sieve. One-gram of each sample was then placed into 50 mL centrifuge tubes, to which 20 mL of 0.01M KCl solution were added. The samples were placed on a mechanical shaker and removed after 0.05 to 4 h, and immediately filtered using disposable syringe filters. Phosphorus released into solution was analyzed on a Technicon Auto Analyzer II using the ascorbic acid method (Murphy and Riley, 1962).

Model fitting. Sorption data were fitted to a first order type of kinetic equation (Sparks, 1985). This model assumes that the rate of adsorption of an ion onto a colloidal surface is proportional to the quantity of the ion remaining in solution. A first order equation is expressed as

$$d(C_o\text{-}C)/dt = kt \qquad (4\text{-}3)$$

where C is the concentration of P in the soil solution at time t, $C_o$ is the initial concentration of P added at time zero, and k is the adsorption rate constant.

Upon integration, the equation becomes

$$\ln C = \ln C_o - kt \qquad (4\text{-}4)$$

A plot of lnC versus t should yield a straight line with a slope equal to -k and an intercept of $\ln C_o$.

Desorption data were fitted to a modified Elovich equation (Chien and Clayton, 1980) of the form

$$P_d = (1/\beta) \ln (\alpha\beta) + (1/\beta) \ln t \qquad (4\text{-}5)$$

where $P_d$ is the amount of P desorbed at time t, $\alpha$, and $\beta$ are constants. A plot of $P_d$ versus lnt should yield a straight line with a slope equal to $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$. The constants $\alpha$ and $\beta$ are used to compare the reaction rates of P release or sorption in different soils. According to Eqn. 4-5, a decrease of $\beta$ and/or an increase of $\alpha$ should enhance the reaction rate.

Statistical Analyses

General Linear Models procedure was used to examine significance of the effect of pH on the forms and distribution of Fe and Al, and P in the soils. Mean comparisons were done by Duncan's Multiple Range Test. Relationships of the different P sorption parameters with soil properties were established using simple correlation analysis.

Phosphate Mineral Equilibria

The stability of Fe and Al phosphates in the spodic samples was evaluated using the solubility product principle. The computer program SOILCHEM (Sposito and Coves, 1991) was used to calculate the speciation of chemical elements in the soil solution. Soil solution chemistry data were obtained by 24-h extraction of P-amended and unamended soils at various pH levels with 0.01M KCl using a 1:2 soil:solution ratio. Input data consisted of the measured concentrations of Ca, Mg, Fe, Al, P, and pH. Ionic strength

was estimated from the electrical conductivity of the solutions. The program was run with no solids allowed to form, but any solid may precipitate if the solution is saturated with respect to it. Calculated ion activities were corrected for various ion pairs and complexes.

## Results

### Physico-chemical Properties of the Soils

The soils were highly acidic, and based on their ΔpH values bore net negative charge under natural conditions (Table 4-2). Although both soils were Al-dominated, Wauchula had far greater Al than Fe compared to EauGallie. The mole ratio of total Al to Fe was 45:1 for Wauchula and 2:1 for EauGallie. In both soils, Al was present largely in amorphous form (Oxal-Al) and in association with organic matter (Pyro-Al and $CuCl_2$-Al). A small fraction of total Al was exchangeable (KCl-Al). The high levels of extractable Fe in EauGallie were a reflection of its total Fe content.

Total P in the soils was small. Phosphorus associated with Fe and Al dominated the inorganic P pool of the soils (NaOH-$P_i$) (Table 4-2). A larger fraction of the total P was bound to organic matter (NaOH-$P_o$). Loosely bound P ($NH_4Cl$-P) and Ca-P (HCl-P) were practically absent.

The soils contained predominantly sand-size particles. The clay fraction of the soils was dominated by quartz (Fig. 4-1) with variably low amounts of silicate minerals.

Table 4-2. Initial physico-chemical properties of the soils studied.

| Soil Property | EauGallie | Wauchula |
|---|---|---|
| $pH_{H2O}$ | 4.3 | 4.6 |
| $pH_{KCl}$ | 3.4 | 3.8 |
| ΔpH | -0.9 | -0.8 |
| Organic C, g $kg^{-1}$ | 14.9 | 19.9 |
| Clay content, % | 4.1 | 7.1 |
| Exch. Bases, $mmol_{(+)}kg^{-1}$ | | |
| Ca | 1.92 | 1.70 |
| Mg | 2.84 | 0.67 |
| K | 0.28 | 0.28 |
| Na | 0.74 | 0.44 |
| Extractable Al, mmol $kg^{-1}$ | | |
| $CuCl_2$-Al | 18.19 | 118.48 |
| Oxal-Al | 23.74 | 161.55 |
| Pyro-Al | 22.06 | 167.89 |
| CDB-Al | 24.97 | 168.68 |
| KCl-Al | 5.68 | 7.13 |
| Total Al | 32.15 | 208.67 |
| Extractable Fe, mmol $kg^{-1}$ | | |
| Oxal-Fe | 15.25 | 1.43 |
| Pyro-Fe | 12.20 | 1.81 |
| CDB-Fe | 15.35 | 2.17 |
| Total Fe | 16.04 | 4.84 |
| P Fractions, mmol $kg^{-1}$ | | |
| $NH_4Cl$-P | 0.00 | 0.00 |
| NaOH-$P_i$ | 0.40 | 0.18 |
| NaOH-$P_o$ | 0.41 | 1.15 |
| HCl-P | 0.01 | 0.01 |
| Total P | 1.40 | 2.51 |

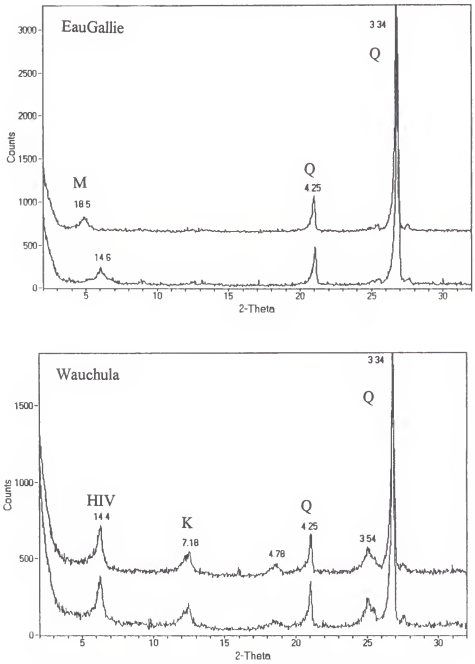



Fig. 4-1. X-ray diffraction patterns for the clay fractions of EauGallie and Wachula soils. M is montmorillonite, HIV is hydroxy-interlayered vermicullite, K is kaolinite and Q is quartz.

Montmorillonite was identified in EauGallie while kaolinite and hydroxy-interlayered vermicullite (HIV) were detected in Wauchula.

The colloidal fraction of the soils was dominated by variable charge materials whose charge depended on pH and electrolyte concentration of the soil solution. The pH value at which the net surface charge underwent reversal (PZSE) was 3.30 for EauGallie (Fig. 4-2) and 4.05 for Wauchula (Fig. 4-3). This indicates that under natural conditions these soils carry a net negative charge. The negative charges in the soils increased with pH (Table 4-3). Conversely, the positive charges decreased as pH increased. At pH>5.0, all sites are negatively charged. On a whole soil basis, Wauchula exhibited higher negative charge than EauGallie (Table 4-3). However, when these values are expressed with respect to their specific surface, EauGallie exhibited greater charge on an areal basis at a given pH than Wauchula. Loading P into the soils, displaced the PZSE to lower pH values (Fig. 4-2; 4-3), thereby increasing CEC and net negative charge of the soils (Table 4-3).

Extractability of Al and Fe as Influenced by pH

Manipulation of soil pH affected the size of some Fe and Al pools in the soils (Table 4-4). For both soils, KCl-Al and oxalate-extractable Al significantly decreased with increasing pH. The extractability of Al in EauGallie by $CuCl_2$ reagent increased with increasing acidity. The solubility of Al in CDB and pyrophosphate reagents in both soils was generally unaffected by changes in pH. The effect of pH adjustment on the various pools of Fe in both soils was small and somewhat variable.

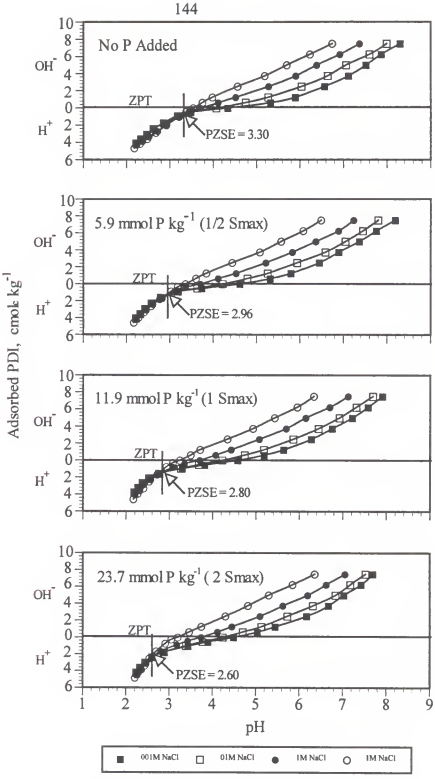



Fig. 4-2. Shifts in PZSE for Eaugallie soil as influenced by P loading. PZSE is point of zero salt effect.

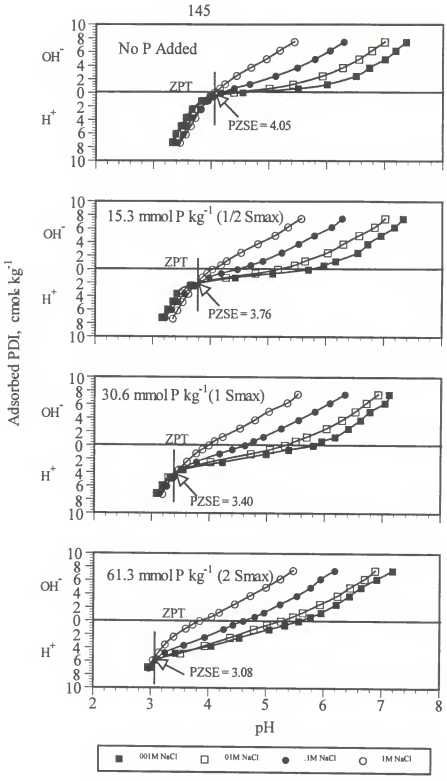



Fig. 4-3. Shifts in PZSE for Wauchula soil as influenced by P loading. PZSE is point of zero salt effect.

Table 4-3. Distribution of positive and negative charges in the soils at various pH and P levels as determined by direct adsorption of $Na^+$ and $Cl^-$ in 0.01M NaCl. AEC is anion exchange capacity; CEC is cation exchange capacity; Net charge is AEC-CEC.

| Soil | P-Level[§] | pH[¶] | AEC $cmol_{(-)}kg^{-1}$ | CEC $cmol_{(+)}kg^{-1}$ | Net Charge $cmol_{(\pm)}kg^{-1}$ | Surface Charge Density $cmol\ cm^{-2} \times 10^{-5}$ |
|---|---|---|---|---|---|---|
| EauGallie | 0 | 3.5 | 0.380 | 0.435 | -0.055 | -0.34 |
| | | 3.9 | 0.251 | 0.558 | -0.307 | -1.91 |
| | | 5.0 | 0.016 | 1.031 | -1.014 | -6.30 |
| | | 6.0 | 0.000 | 1.632 | -1.632 | -10.13 |
| | ½ $S_{max}$ | 3.5 | 0.367 | 0.527 | -0.160 | -0.99 |
| | | 3.9 | 0.223 | 0.738 | -0.514 | -3.19 |
| | | 5.0 | 0.000 | 1.331 | -1.331 | -8.26 |
| | | 6.0 | 0.000 | 1.889 | -1.889 | -11.73 |
| | 1 $S_{max}$ | 3.5 | 0.360 | 0.506 | -0.146 | -0.91 |
| | | 3.9 | 0.227 | 0.710 | -0.484 | -3.00 |
| | | 5.0 | 0.000 | 1.322 | -1.322 | -8.21 |
| | | 6.0 | 0.000 | 1.944 | -1.944 | -12.07 |
| | 2 $S_{max}$ | 3.5 | 0.292 | 0.464 | -0.172 | -1.07 |
| | | 3.9 | 0.190 | 0.645 | -0.455 | -2.82 |
| | | 5.0 | 0.003 | 1.280 | -1.276 | -7.92 |
| | | 6.0 | 0.000 | 2.034 | -2.034 | -12.63 |
| Wauchula | 0 | 3.5 | 0.864 | 0.001 | 0.864 | 1.05 |
| | | 4.1 | 0.431 | 0.153 | 0.278 | 0.34 |
| | | 5.0 | 0.005 | 1.056 | -1.051 | -1.28 |
| | | 6.0 | 0.000 | 3.022 | -3.022 | -3.68 |
| | ½ $S_{max}$ | 3.5 | 0.878 | 0.145 | 0.733 | 0.89 |
| | | 4.1 | 0.354 | 0.198 | 0.156 | 0.19 |
| | | 5.0 | 0.000 | 0.910 | -0.910 | -1.11 |
| | | 6.0 | 0.000 | 2.590 | -2.590 | -3.15 |
| | 1 $S_{max}$ | 3.5 | 0.602 | 0.135 | 0.468 | 0.57 |
| | | 4.1 | 0.359 | 0.400 | -0.041 | -0.05 |
| | | 5.0 | 0.103 | 1.415 | -1.312 | -1.60 |
| | | 6.0 | 0.000 | 3.410 | -3.410 | -4.15 |
| | 2 $S_{max}$ | 3.5 | 0.837 | 0.373 | 0.464 | 0.56 |
| | | 4.1 | 0.535 | 0.923 | -0.389 | -0.47 |
| | | 5.0 | 0.204 | 2.275 | -2.072 | -2.52 |
| | | 6.0 | 0.009 | 4.520 | -4.512 | -5.49 |

[§] These rates are equivalent to 5.93, 11.85, and 23.70 mmol P $kg^{-1}$ for Eaugallie. For Wauchula these levels correspond to 15.33, 30.65, and 61.30 mmol P $kg^{-1}$.

[¶] pH in 0.01M KCl.

Table. 4-4. The forms and distribution of Fe and Al in the spodic horizons at various pH levels. (KCl is potassium chloride; $CuCl_2$ is cupric chloride; Oxal is ammonium oxalate; CDB is citrate-dithionite-bicarbonate; Pyro is sodium pyrophosphate). Values are expressed in mmol $kg^{-1}$ of soil.

| Soil | pH | KCl-Al | $CuCl_2$-Al | Oxal-Al | CDB-Al | Pyro-Al | Oxal-Fe | CDB-Fe | Pyro-Fe |
|---|---|---|---|---|---|---|---|---|---|
| EauGallie | 3.5 | 6.04*a*[1] | 16.49*a* | 24.70*a* | 24.07*a* | 24.25*a* | 14.96*a* | 13.64*a* | 14.15*a* |
| | 3.9 | 5.17*b* | 16.02*ab* | 23.90*ab* | 23.91*a* | 24.48*a* | 14.50*ab* | 13.51*a* | 14.20*a* |
| | 5.0 | 2.10*c* | 15.98*ab* | 24.79*a* | 24.98*a* | 25.25*a* | 15.03*a* | 14.09*a* | 14.64*a* |
| | 6.0 | 0.20*d* | 15.52*b* | 22.68*b* | 24.10*a* | 23.72*a* | 13.87*a* | 13.71*a* | 13.67*a* |
| Wauchula | 3.5 | 13.06*a* | 94.48*a* | 182.74*a* | 177.13*ab* | 187.58*a* | 1.76*a* | 2.01*ab* | 1.97*a* |
| | 4.1 | 8.17*b* | 98.89*a* | 175.64*b* | 167.73*b* | 178.85*a* | 1.70*ab* | 1.98*b* | 1.94*a* |
| | 5.0 | 4.16*c* | 107.58*a* | 176.92*b* | 184.26*a* | 176.93*a* | 1.68*b* | 2.15*a* | 1.92*a* |
| | 6.0 | 0.58*d* | 100.75*a* | 167.83*c* | 173.65*ab* | 175.01*a* | 1.59*c* | 2.02*ab* | 1.85*a* |

[1] Separation of means at $p<0.05$ by DMRT.

Forms and Distribution of P at Various pH Levels

The effect of pH on the chemical fractionation of P in the spodic samples was small and variable, except for the labile P pool ($NH_4Cl$-P) which appeared to increase as the pH increased (Table 4-5). Phosphorus loading significantly increased the size of all P fractions. In both soils, most of the added P was found largely in the form of Fe/Al-P (NaOH-$P_i$). The increase in size of this fraction was proportional to the amount of P added.

Phosphorus Sorption-Desorption Behavior

Phosphorus sorption. Wauchula exhibited greater capacity to sorb P than EauGallie (Fig. 4-4). The effect of pH was more pronounced in Wauchula than in EauGallie, as the curves became steeper with increasing soil acidity. Sorption at the highest level of P added (3.223 mM P) ranged from over 20 mmol P $kg^{-1}$ at pH 6.0 to about 45 mmol P $kg^{-1}$ at pH 3.5. EauGallie produced flat curves, whose slopes slightly increased as pH decreased. Phosphorus sorption was generally low and did not exceed 10 mmol P $kg^{-1}$ at any point on the isotherm at any given pH.

Phosphorus desorption. The soils exhibited P release properties that depended on pH. At a given pH, the desorbability of P was much greater in EauGallie than in Wauchula. Sequentially desorbed P (expressed as a percentage of initially sorbed P) accounted for over 70% of the freshly sorbed P in EauGallie, a large proportion of which desorbed during the first extraction (Table 4-6). The desorbability of P in this soil increased significantly with an increase in pH, with values ranging from 65% at pH 3.5 to over 70% at higher pH levels.

Table 4-5. Changes in the distribution of the P fractions in the spodic horizon following addition of P at various pH levels. ($NH_4Cl$-P is loosely bound P; NaOH-$P_i$ is Fe/Al-bound P; NaOH-$P_o$ is moderately labile organic P; HCl-P is Ca/Mg-P; Sum is total of all P fractions). Values are expressed in mmol P $kg^{-1}$ of soil.

| Soil | P-Level[‡] | pH | $NH_4Cl$-P | NaOH-$P_i$ | NaOH-$P_o$ | HCl-P | Sum |
|---|---|---|---|---|---|---|---|
| EauGallie | 0 P | 3.5 | 0.00*a*[¶] | 0.37*b* | 0.44*a* | 0.00*a* | 0.81*a* |
| | | 3.9 | 0.00*a* | 0.36bc | 0.42*a* | 0.00*a* | 0.79*a* |
| | | 5.0 | 0.00*a* | 0.35*c* | 0.50*a* | 0.00*a* | 0.86*a* |
| | | 6.0 | 0.00*a* | 0.39*a* | 0.50*a* | 0.00*a* | 0.89*a* |
| | ½ $S_{max}$ | 3.5 | 0.25*c* | 4.97*ab* | 0.26*a* | 0.02*ab* | 5.50*a* |
| | | 3.9 | 0.25*c* | 4.99*a* | 0.42*a* | 0.01*b* | 5.66*a* |
| | | 5.0 | 0.31*b* | 4.97*ab* | 0.43*a* | 0.00*b* | 5.71*a* |
| | | 6.0 | 0.36*a* | 4.85*b* | 0.32*a* | 0.03*a* | 5.56*a* |
| | 1 $S_{max}$ | 3.5 | 1.23*b* | 9.05*a* | 0.70*b* | 0.02*a* | 11.01*a* |
| | | 3.9 | 1.23*b* | 9.13*a* | 1.01*a* | 0.02*a* | 11.39*a* |
| | | 5.0 | 1.31*b* | 8.94*a* | 1.20*a* | 0.03*a* | 11.48*a* |
| | | 6.0 | 1.44*a* | 8.95*a* | 1.25*a* | 0.02*a* | 11.67*a* |
| | 2 $S_{max}$ | 3.5 | 5.82*a* | 14.29*c* | 1.77*a* | 0.05*a* | 21.92*a* |
| | | 3.9 | 5.58*a* | 14.62*bc* | 1.67*a* | 0.06*a* | 21.93*a* |
| | | 5.0 | 5.66*a* | 15.07*a* | 1.68*a* | 0.03*a* | 22.43*a* |
| | | 6.0 | 5.65*a* | 14.71*ab* | 1.87*a* | 0.04*a* | 22.28*a* |
| Wauchula | 0 P | 3.5 | 0.00*a* | 0.20*a* | 1.08*ab* | 0.00*a* | 1.28*ab* |
| | | 4.1 | 0.00*a* | 0.18*a* | 1.00*bc* | 0.00*a* | 1.19*bc* |
| | | 5.0 | 0.00*a* | 0.19*a* | 1.15*a* | 0.00*a* | 1.33*a* |
| | | 6.0 | 0.00*a* | 0.20*a* | 0.96*c* | 0.01*a* | 1.17*c* |
| | ½ $S_{max}$ | 3.5 | 0.16*d* | 13.42c | 2.96*a* | 0.01*a* | 16.55*b* |
| | | 4.1 | 0.19*c* | 14.01*ab* | 2.69*a* | 0.00*a* | 16.90*ab* |
| | | 5.0 | 0.22*b* | 14.46*a* | 2.91*a* | 0.01*a* | 17.59*a* |
| | | 6.0 | 0.26*a* | 13.61*bc* | 3.13*a* | 0.01*a* | 17.02*ab* |
| | 1 $S_{max}$ | 3.5 | 0.59*b* | 29.37*a* | 4.33*a* | 0.05*a* | 34.34*a* |
| | | 4.1 | 0.76*a* | 28.21*b* | 3.71*ab* | 0.03*a* | 32.71*b* |
| | | 5.0 | 0.76*a* | 27.77*b* | 3.43*b* | 0.12*a* | 32.08*b* |
| | | 6.0 | 0.77*a* | 26.40*c* | 3.22*b* | 0.03*a* | 30.42*c* |
| | 2 $S_{max}$ | 3.5 | 4.00*a* | 54.24*a* | 3.18*a* | 0.10*a* | 61.51*a* |
| | | 4.1 | 4.20*a* | 52.93*a* | 3.66*a* | 0.10*a* | 60.88*a* |
| | | 5.0 | 4.03*a* | 53.63*a* | 3.60*a* | 0.08*a* | 61.34*a* |
| | | 6.0 | 3.15*b* | 52.96*a* | 3.81*a* | 0.10*a* | 60.01*a* |

[‡] These rates correspond to 5.93, 11.85, and 23.70 mmol P $kg^{-1}$ for EauGallie.
For Wauchula these rates are equivalent to 15.33, 30.65, and 61.30 mmol P $kg^{-1}$.
[¶] pH-wise comparison of means at $p < 0.05$ by DMRT.

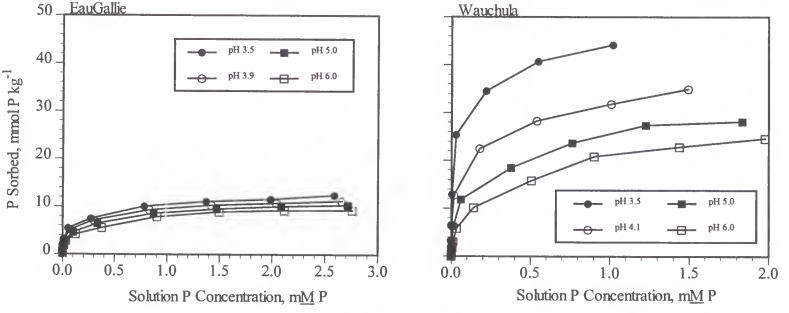



Fig. 4-4. Phosphorus sorption isotherms for EauGallie and Wauchula soils at different pH levels.

Table 4-6. Sequentially desorbed P in the spodic samples at various pH levels.

| Soil | pH | P Desorbed, mmol P $kg^{-1}$ | | | | | | | | | | Desorbed P[¶] % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Initial[§] | Day 1 | Day 2 | Day 3 | Day 4 | Day 5 | Day 6 | Day 9 | Day 8 | Day 9 | |
| EauGallie | 3.5 | 12.39 | 3.81 | 1.51 | 0.88 | 0.55 | 0.42 | 0.30 | 0.26 | 0.22 | 0.20 | 65.75*b*[†] |
| | 3.9 | 11.19 | 3.55 | 1.52 | 0.83 | 0.48 | 0.38 | 0.27 | 0.24 | 0.19 | 0.17 | 68.19*ab* |
| | 5.0 | 9.20 | 2.70 | 1.52 | 0.89 | 0.51 | 0.37 | 0.25 | 0.24 | 0.17 | 0.15 | 74.05*a* |
| | 6.0 | 9.20 | 2.90 | 1.31 | 0.79 | 0.54 | 0.34 | 0.24 | 0.22 | 0.16 | 0.15 | 72.16*a* |
| Wauchula | 3.5 | 43.41 | 3.73 | 1.84 | 1.24 | 0.94 | 0.81 | 0.68 | 0.63 | 0.58 | 0.55 | 25.38*d* |
| | 4.1 | 34.63 | 3.90 | 2.01 | 1.16 | 0.76 | 0.55 | 0.40 | 0.34 | 0.28 | 0.25 | 27.85*c* |
| | 5.0 | 30.06 | 3.42 | 1.89 | 1.20 | 0.73 | 0.57 | 0.44 | 0.38 | 0.33 | 0.29 | 30.80*b* |
| | 6.0 | 20.66 | 2.83 | 1.47 | 0.90 | 0.63 | 0.40 | 0.30 | 0.26 | 0.23 | 0.20 | 34.99*a* |

[§] Start value for sorbed P.

[¶] Expressed as percent of initially sorbed P.

[†] pH-wise comparison at $p<0.05$ by DMRT.

On the contrary, Wauchula showed desorption behavior that may continue for some time. Desorbability of P in this soil was very slow. After nine 24-h successive extractions, an average of only about 30% of the sorbed P was released into solution. Soil pH significantly increased P release potential of this soil. Values ranged from a little over 25% at pH 3.5 to about 35% at pH 6.0.

Phosphorus sorption in Wauchula was highly irreversible (Fig. 4-5). About 70% of the added P remained in the adsorbed phase after nine extractions compared to just about 20% in EauGallie. The effect of pH on the recovery of added P in both soils was consistently small.

Phosphorus Sorption Parameters

Sorption data were fitted by regression analyses to the linear form of Langmuir and Freundlich equations. The overall fit of the data to the models was very good. However, based on the $r^2$ values, sorption of P by the soils was better described by the Langmuir than by Freundlich equation (Table 4-7). This model gave $r^2$ values close to unity in both soils across all pH values. The Freundlich model described P sorption in EauGallie better than in Wauchula.

The soils exhibited different affinities for P that decreased with an increase in pH. Phosphorus sorption capacities ($S_{max}$) for EauGallie ranged from 9.5 mmol P $kg^{-1}$ at pH 6.0 to 12 mmol P $kg^{-1}$ at pH 3.5 (Table 4-7). Wauchula sorbed far more P than EauGallie. Maximum sorption capacities for this soil were between 27 mmol P $kg^{-1}$ at pH 6.0 and 44 mmol P $kg^{-1}$ at pH 3.5. For both soils, the highest increase in $S_{max}$ values

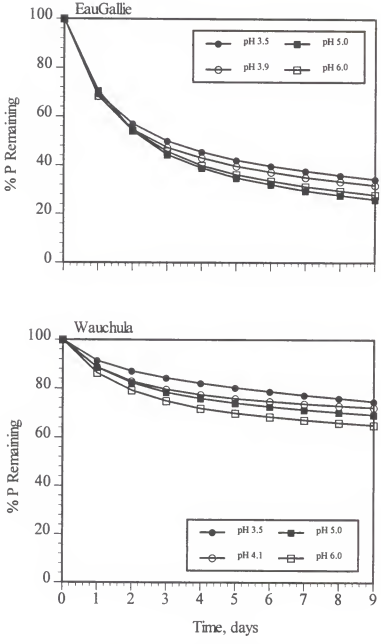



Fig. 4-5. Desorbability of P in the spodic horizon as influenced by pH. The values on the y-axis represent the amount of P remaining in the soil expressed as a percentage of initially adsorbed P.

Table 4-7. Equilibrium P concentrations (EPC) and phosphorus sorption parameters for the spodic horizons obtained from the linear Langmuir and Freundlich equations. $S_{max}$ is Langmuir sorption maximum; b is Langmuir constant related to P binding energy; MBC is maximum P buffer capacity; K and n are Freundlich constants; $r^2$ is regression coefficient.

| Soil | pH | EPC | Langmuir | | | | Freundlich | | |
|---|---|---|---|---|---|---|---|---|---|
| | | μM P | $S_{max}$ mmol P $kg^{-1}$ | b L $mmol^{-1}$ P | MBC L $kg^{-1}$ | $r^2$ | K mmol P $kg^{-1}$ | n L $kg^{-1}$ | $r^2$ |
| EauGallie | 3.5 | 0.14 | 12.06 | 21 | 257 | 0.994 | 12.38 | 0.49 | 0.932 |
| | 3.9 | 0.10 | 10.98 | 25 | 273 | 0.996 | 10.60 | 0.41 | 0.961 |
| | 5.0 | 0.70 | 10.27 | 16 | 162 | 0.995 | 9.24 | 0.45 | 0.957 |
| | 6.0 | 2.23 | 9.47 | 10 | 99 | 0.995 | 8.13 | 0.49 | 0.949 |
| Wauchula | 3.5 | 0.00 | 43.63 | 77 | 3343 | 0.996 | 90.02 | 0.54 | 0.842 |
| | 3.9 | 0.00 | 33.71 | 57 | 1913 | 0.993 | 41.06 | 0.41 | 0.882 |
| | 5.0 | 0.10 | 30.18 | 7 | 196 | 0.924 | 30.30 | 0.53 | 0.886 |
| | 6.0 | 0.34 | 26.79 | 4 | 115 | 0.951 | 23.12 | 0.56 | 0.916 |

was observed when pH was lowered to 3.5. By adjusting soil pH to 3.5, $S_{max}$ increased by almost 30% for Wauchula and 10% for EauGallie.

The binding energy (b) values of the soils at different pH levels were consistent with the $S_{max}$ values (Table 4-7). The b values for EauGallie ranged from 10 L $mmol^{-1}$ P at pH 6.0 to 21 L $mmol^{-1}$ P at pH 3.5. The range in b values for Wauchula was much wider; from 4 to 77 L $mmol^{-1}$ P at pH 3.5 and 6.0, respectively.

Wauchula exhibited maximum buffer capacities (MBC) much higher than EauGallie (Table 4-7). With decreasing pH, these values ranged from 115 to 3343 L $kg^{-1}$ in Wauchula and from 99 to 257 L $kg^{-1}$ in EauGallie.

The Freundlich constant K, also known as the adsorption coefficient showed a trend similar to $S_{max}$, one that increased with a decrease in pH (Table 4-7). The constant n values were similar for both soils and were unaffected by changes in soil pH.

Kinetics of Phosphorus Sorption-Desorption

Phosphorus sorption. Sorption of P was characterized by an initially rapid reaction which became increasingly slow with time. For both soils, sorption rate decreased with increasing pH and initial P concentration. The sorption data as a whole for both soils failed to conform to first order kinetics. However, from the plot of the data, it was apparent that sorption of P by the soils can be described by two first order equations (Fig. 4-6; 4-7). Region I defines the rapid reaction during the first 4-h while Region II corresponds to the slower reaction that followed. Based on the $r^2$ values, the first order equation adequately described the rapid and slow sorption of P by the soils (Table 4-8).

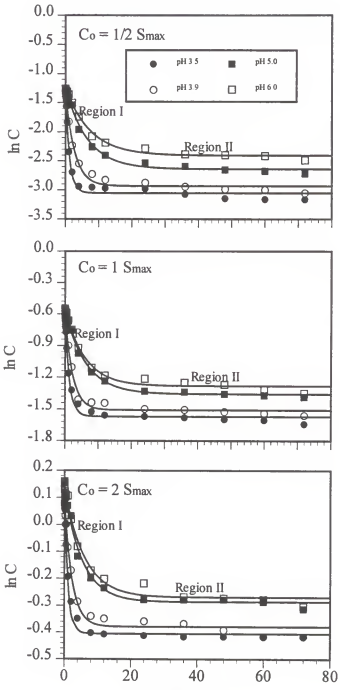



Fig. 4-6. Plot of first order equation for P sorption in EauGallie at different pH levels and initial solution P concentrations ($C_o$). C is the concentration of P remaining in solution at time t. $C_o$ values correspond to 0.30, 0.59, and 1.18 mM P.

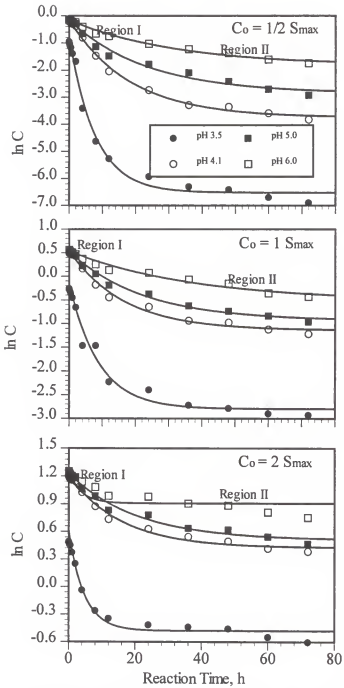



Fig. 4-7. Plot of first order equation for P sorption in Wauchula at various pH levels and initial solution P concentrations (Co). C is the concentration of P remaining in solution at time t. Co values correspond to 0.77, 1.53, and 3.06 mM P.

Table 4-8. First order rate constants obtained for sorption of P by EauGallie and Wauchula soils at various pH levels and initial P concentrations ($C_o$). $k_f$ and $k_s$ represent the rapid and slow reactions, respectively; $r^2$ is regression coefficient.

| Soil | $C_o$[§], mM P | pH | $k_f$, $h^{-1}$ | $r^2$ | $k_s$, $h^{-1}$ | $r^2$ |
|---|---|---|---|---|---|---|
| EauGallie | ½ $S_{max}$ | 3.5 | 0.4455 | 0.857 | 0.0038 | 0.923 |
| | | 3.9 | 0.3329 | 0.944 | 0.0044 | 0.914 |
| | | 5.0 | 0.1645 | 0.985 | 0.0064 | 0.861 |
| | | 6.0 | 0.1178 | 0.989 | 0.0056 | 0.877 |
| | 1 $S_{max}$ | 3.5 | 0.2249 | 0.837 | 0.0015 | 0.931 |
| | | 3.9 | 0.2088 | 0.966 | 0.0019 | 0.935 |
| | | 5.0 | 0.0958 | 0.982 | 0.0030 | 0.750 |
| | | 6.0 | 0.0924 | 0.992 | 0.0032 | 0.937 |
| | 2 $S_{max}$ | 3.5 | 0.1264 | 0.812 | 0.0002 | 0.732 |
| | | 3.9 | 0.1010 | 0.894 | 0.0013 | 0.964 |
| | | 5.0 | 0.0588 | 0.946 | 0.0014 | 0.771 |
| | | 6.0 | 0.0553 | 0.959 | 0.0019 | 0.907 |
| Wauchula | ½ $S_{max}$ | 3.5 | 0.6091 | 0.890 | 0.0314 | 0.877 |
| | | 3.9 | 0.1421 | 0.951 | 0.0336 | 0.879 |
| | | 5.0 | 0.1126 | 0.927 | 0.0268 | 0.983 |
| | | 6.0 | 0.0590 | 0.968 | 0.0170 | 0.988 |
| | 1 $S_{max}$ | 3.5 | 0.3233 | 0.735 | 0.0186 | 0.746 |
| | | 3.9 | 0.0847 | 0.919 | 0.0150 | 0.919 |
| | | 5.0 | 0.0704 | 0.925 | 0.0147 | 0.942 |
| | | 6.0 | 0.0441 | 0.965 | 0.0130 | 0.982 |
| | 2 $S_{max}$ | 3.5 | 0.1667 | 0.862 | 0.0046 | 0.940 |
| | | 3.9 | 0.0423 | 0.861 | 0.0070 | 0.920 |
| | | 5.0 | 0.0395 | 0.895 | 0.0072 | 0.929 |
| | | 6.0 | 0.0274 | 0.915 | 0.0045 | 0.953 |

[§] Equivalent to initial P concentrations ($C_o$) of 0.30, 0.59, and 1.18 mM P for EauGallie. For Wauchula, these rates correspond to 0.77, 1.53, and 3.06 mM P, respectively.

Sorption rates for the fast reaction ($k_f$) in both soils, increased with decreasing pH and initial P concentration (Table 4-8). The $k_f$ values for EauGallie varied from 0.055 $h^{-1}$ at pH 6.0 and $C_o$=2 $S_{max}$ to 0.446 $h^{-1}$ at pH 3.5 and $C_o$=1/2 $S_{max}$. The $k_f$ values for Wauchula at the same pH and $C_o$ ranged from 0.027 to 0.609 $h^{-1}$. Reaction rate was highest in Wauchula at pH 3.5 and at the lowest $C_o$. The $k_f$ value of EauGallie in most cases, was higher than Wauchula at pH above 3.5. Sorption rates for the slow reaction ($k_s$) were several fold lower than $k_f$. These values were generally higher for Wauchula than EauGallie across all pH and $C_o$ levels.

Phosphorus desorption. The Elovich equation gave a very good description of the 4-h desorption reaction in both soils (Fig. 4-8; 4-9). Regression coefficients ($r^2$) of over 0.90 were found across all pH and $C_o$ levels for EauGallie (Table 4-9). By comparison, description of P desorption by the equation for Wauchula was just as good but not as consistent, especially at the highest $C_o$.

The calculated values of $\alpha$ and $\beta$ varied with both pH and $C_o$ levels (Table 4-9). In both soils, the values for $\alpha$ increased with increasing $C_o$. Values were generally higher for EauGallie than Wauchula at all $C_o$ levels. The values for EauGallie ranged from 2.5 (at pH 5.0 and $C_o$=1/2 $S_{max}$) to 84 mmol P $kg^{-1}$ $h^{-1}$ (at pH 6.0 and $C_o$=2 $S_{max}$). For Wauchula, $\alpha$ values varied from 1.2 to 27 at the same pH and $C_o$ levels.

The effect of pH on $\alpha$ was quite variable particularly at lower $C_o$ levels. At the highest $C_o$, however, an apparent increasing trend with pH was observed. Values for $\beta$ as predicted by Eqn. 4-5 decreased as $\alpha$ increased. For both soils, values for $\beta$ were highest at the lowest $C_o$, where the effect of pH was most evident.

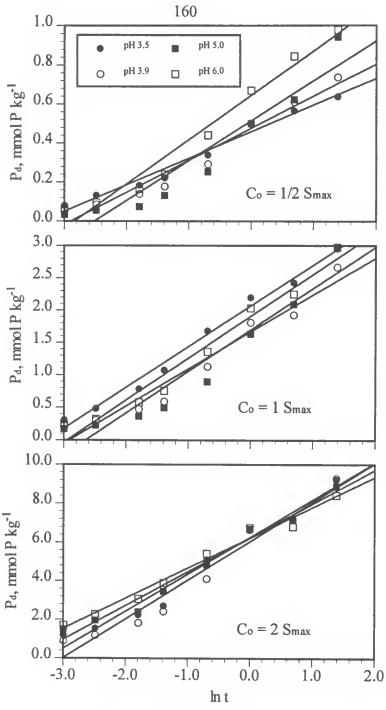



Fig. 4-8. Plot of Elovich equation for P desorption in EauGallie at different pH levels and initial solution P concentrations ($C_o$). $P_d$ is the amount of P desorbed at time t (h); $C_o$ values correspond to 5.93, 11.85, and 23.70 mmol P $kg^{-1}$

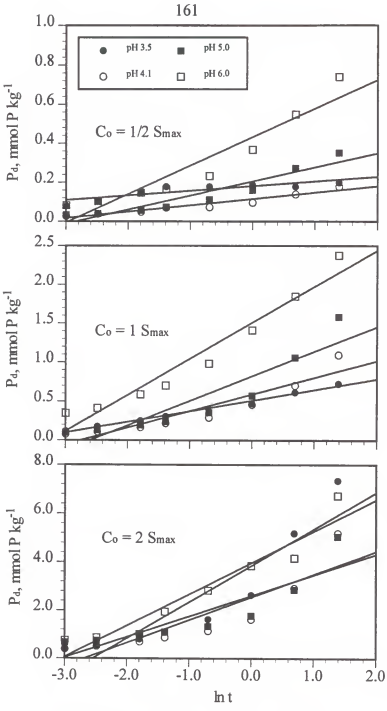



Fig. 4-9. Plot of Elovich equation for P desorption in Wauchula at different pH levels and initial solution P concentrations ($C_o$). $P_d$ is the amount of P desorbed at time t (h); $C_o$ values correspond to 15.33, 30.65, and 61.30 mmol P $kg^{-1}$

Table 4-9. Calculated values of α and β of the Elovich equation for P desorption in EauGallie and Wauchula soils as influenced by pH and amount of initially added P. Calculations were obtained from a 4-h reaction time. $r^2$ is regression coefficient.

| Soil | P Added[§] mmol P $kg^{-1}$ | pH | α mmol $kg^{-1}$ $h^{-1}$ | β (mmol P $kg^{-1}$)$^{-1}$ | $r^2$ |
|---|---|---|---|---|---|
| EauGallie | ½ $S_{max}$ | 3.5 | 3.95 | 7.34 | 0.978 |
| | | 3.9 | 2.98 | 6.08 | 0.958 |
| | | 5.0 | 2.53 | 4.89 | 0.906 |
| | | 6.0 | 3.88 | 4.40 | 0.967 |
| | 1 $S_{max}$ | 3.5 | 16.78 | 1.59 | 0.988 |
| | | 3.9 | 10.51 | 1.75 | 0.950 |
| | | 5.0 | 9.05 | 1.56 | 0.920 |
| | | 6.0 | 12.31 | 1.55 | 0.968 |
| | 2 $S_{max}$ | 3.5 | 50.19 | 0.52 | 0.968 |
| | | 3.9 | 40.69 | 0.50 | 0.960 |
| | | 5.0 | 61.25 | 0.57 | 0.976 |
| | | 6.0 | 84.37 | 0.64 | 0.981 |
| Wauchula | ½ $S_{max}$ | 3.5 | 4.04 | 46.08 | 0.833 |
| | | 4.1 | 1.10 | 30.49 | 0.935 |
| | | 5.0 | 1.23 | 13.84 | 0.897 |
| | | 6.0 | 2.81 | 6.84 | 0.902 |
| | 1 $S_{max}$ | 3.5 | 5.67 | 7.33 | 0.987 |
| | | 4.1 | 3.36 | 4.69 | 0.873 |
| | | 5.0 | 4.25 | 3.17 | 0.841 |
| | | 6.0 | 11.95 | 2.15 | 0.949 |
| | 2 $S_{max}$ | 3.5 | 19.25 | 0.66 | 0.845 |
| | | 4.1 | 13.82 | 1.06 | 0.790 |
| | | 5.0 | 17.85 | 1.17 | 0.781 |
| | | 6.0 | 27.33 | 0.77 | 0.920 |

[§] These rates correspond to 5.93, 11.85, and 23.70 mmol P $kg^{-1}$ for EauGallie. For Wauchula, these values correspond to 15.33, 30.65, and 61.30 mmol P $kg^{-1}$.

## Discussion

The two spodic samples differed widely in their ability to sorb added P. Under natural conditions, Wauchula exhibited a maximum P sorption capacity ($S_{max}$) of 34 mmol P $kg^{-1}$ compared to just 11 mmol P $kg^{-1}$ for EauGallie. An examination of the initial chemical properties of the soils indicated that the large differences in their Fe and Al contents, more than any other factor accounted for the different P sorption behavior of the soils. The combined Fe and Al content of the soils were 214 and 48 mmol $kg^{-1}$ for Wauchula and EauGallie, respectively. Aluminum more than Fe contributed to P sorption in these soils. This was expected as Al dominated the colloidal fraction of these soils. Concentrations of Fe in the spodic horizons from Florida Spodosols are generally low and would not be expected to contribute significantly to P sorption. In EauGallie, exchangeable Al (KCl-Al) and organically bound Al ($CuCl_2$-Al) gave significant correlations with all P sorption parameters (Table 4-10). In Wauchula, both the exchangeable Al and amorphous Al and Fe (Oxal-extractable) were most active in P sorption (Table 4-11). The significant correlation of Fe with P sorption was somewhat surprising, considering that the Fe content of this soil relative to Al was very small. Recall that the mole ratio of Al to Fe in this soil was 45:1. Whether this was a true reflection of the association between Fe and P sorption or just an artifact of having a small number of observations in the correlation (n=12) was difficult to tell. However, when data from both soils were used in the correlation (n=24), Fe did not appear to be important. The crystalline forms of Fe and Al did not show any correlation with P

Table 4-10. Correlation of P sorption and desorption parameters with soil properties obtained for EauGallie soil (n=12).

| Soil Property | Langmuir | | | Freundlich | | First order constants | | Desorption constants | | Sequentially Desorbed P |
|---|---|---|---|---|---|---|---|---|---|---|
| | $S_{max}$ | b | MBC | K | n | $k_f$ | $k_s$ | α | β | |
| pH | -0.961*** | -0.916*** | -0.964*** | -0.960*** | 0.366 | -0.954*** | 0.895*** | 0.830*** | -0.953*** | 0.661* |
| $CuCl_2$-Al | 0.730** | 0.581* | 0.651* | 0.738* | -0.065 | 0.652* | -0.654* | -0.480 | 0.686* | -0.435 |
| CDB-Al | -0.219 | -0.200 | -0.226 | -0.223 | -0.049 | -0.344 | 0.342 | 0.055 | -0.296 | 0.644* |
| CDB-Fe | -0.252 | -0.259 | -0.277 | -0.249 | 0.050 | -0.364 | 0.345 | 0.152 | -0.317 | 0.606* |
| CDB-Al+Fe | -0.231 | -0.222 | -0.245 | -0.232 | -0.011 | -0.352 | 0.344 | 0.091 | -0.304 | 0.631* |
| KCl-Al | 0.957*** | 0.915*** | 0.962*** | 0.958*** | -0.347 | 0.971*** | -0.913*** | -0.810** | 0.963*** | -0.701* |
| Oxal-Al | 0.555 | 0.406 | 0.434 | 0.513 | -0.199 | 0.367 | -0.342 | -0.494 | 0.418 | -0.410 |
| Oxal-Fe | 0.515 | 0.364 | 0.390 | 0.474 | -0.169 | 0.329 | -0.309 | -0.449 | 0.380 | -0.399 |
| Oxal-Al+Fe | 0.542 | 0.391 | 0.419 | 0.500 | -0.188 | 0.354 | -0.331 | -0.478 | 0.405 | -0.407 |
| Pyro-Al | 0.095 | 0.148 | 0.146 | 0.080 | -0.325 | -0.034 | 0.089 | -0.302 | -0.013 | 0.110 |
| Pyro-Fe | 0.188 | 0.218 | 0.224 | 0.174 | -0.322 | 0.052 | 0.000 | -0.356 | 0.077 | 0.031 |
| Pyro-Al+Fe | 0.132 | 0.175 | 0.176 | 0.116 | -0.325 | -0.001 | 0.055 | -0.323 | 0.022 | 0.079 |

*, **, *** Denote significance at $p<0.05$, $p<0.01$ and $p<0.001$, respectively.

Table 4-11. Correlation of P sorption and desorption parameters with soil properties obtained for Wauchula soil (n=12).

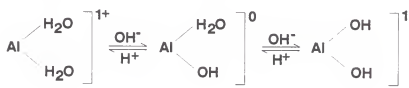
| Soil Property | Langmuir | | | Freundlich | | First order constants | | Desorption constants | | Sequentially Desorbed P |
|---|---|---|---|---|---|---|---|---|---|---|
| | $S_{max}$ | b | MBC | K | n | $k_f$ | $k_s$ | $\beta$ | $\beta$ | |
| pH | -0.923*** | -0.938*** | -0.925*** | -0.853*** | 0.810** | -0.787** | -0.923*** | 0.645* | -0.970*** | 0.984*** |
| $CuCl_2$-Al | -0.427 | -0.474 | -0.485 | -0.433 | 0.390 | -0.426 | -0.207 | -0.068 | -0.445 | 0.286 |
| CDB-Al | -0.007 | -0.288 | -0.207 | 0.014 | 0.469 | 0.082 | -0.143 | 0.034 | -0.131 | 0.116 |
| CDB-Fe | -0.247 | -0.436 | -0.401 | -0.251 | 0.468 | -0.206 | -0.158 | -0.079 | -0.321 | 0.221 |
| CDB-Al+Fe | -0.010 | -0.290 | -0.210 | 0.011 | 0.471 | 0.079 | -0.144 | 0.033 | -0.134 | 0.118 |
| KCl-Al | 0.975** | 0.953*** | 0.967*** | 0.931*** | -0.749** | 0.880*** | 0.837*** | -0.498 | 0.993*** | -0.967*** |
| Oxal-Al | 0.818** | 0.674* | 0.710** | 0.767** | -0.459 | 0.749** | 0.723** | -0.526 | 0.786** | -0.841*** |
| Oxal-Fe | 0.836*** | 0.761** | 0.775** | 0.772** | -0.606* | 0.727** | 0.793** | -0.573 | 0.836*** | -0.875*** |
| Oxal-Al+Fe | 0.819** | 0.676* | 0.711* | 0.768** | -0.461 | 0.749** | 0.724** | -0.528 | 0.788** | -0.842*** |
| Pyro-Al | 0.523 | 0.443 | 0.482 | 0.518 | -0.287 | 0.498 | 0.342 | -0.146 | 0.490 | -0.382 |
| Pyro-Fe | 0.361 | 0.335 | 0.341 | 0.326 | -0.304 | 0.294 | 0.383 | -0.302 | 0.367 | -0.319 |
| Pyro-Al+Fe | 0.522 | 0.443 | 0.482 | 0.517 | -0.288 | 0.497 | 0.343 | -0.148 | 0.490 | -0.383 |

*, **, *** Denote significance at $p<0.05$, $p<0.01$ and $p<0.001$, respectively.

sorption in both soils. This was expected, as crystalline Fe and Al hydrous oxides generally sorb 10-100 times less P than their amorphous analogs (Ryden and Pratt,1980). Several investigators have reported that KCl-extractable Al provided the best index of P retention in soil (Coleman et al., 1960; Syers et al., 1971; Udo and Uzu, 1972).

Manipulation of soil pH altered the P sorption capacities of the soils. Phosphate adsorption showed a steady decrease in maximum adsorption with increasing pH value. The effect of pH on P sorption parameters was more pronounced in Wauchula than in EauGallie (Table 4-7).

The increase in P sorption with increasing pH typifies an adsorption mechanism controlled primarily by noncrystalline Fe and Al oxides (Goldberg and Sposito, 1984). In acid soils, P is specifically adsorbed onto hydroxylated mineral surfaces by a ligand exchange mechanism (Rajan et al., 1974; Parfitt, 1978; Hingston, 1981; Sposito, 1984; Parfitt, 1989). The extent of this reaction depends on the net charge on the surface of the mineral. Due to their amphoteric behavior, Fe and Al oxides exhibit a net negative, net positive, or net zero charge, depending on the pH and ionic strength of the soil solution. The pH value that defines the condition at which the net surface charge on the colloid is zero is called the point of zero charge (PZC). The surface will be positive for $pH<pH_{zpc}$ and negative for $pH>pH_{zpc}$. For an Al oxide surface this behavior can be illustrated as follows:



At the point of zero charge, there are equal numbers of aquo and hydroxo groups on the surface. For the spodic samples used in this study, this condition was attained at pH 3.40 for EauGallie (Fig. 4-10) and 4.35 for Wauchula (Fig. 4-11). Therefore, under the range of pH used in the study, EauGallie would have a net negative charge that increases with pH while Wauchula would maintain a net positive charge up to pH 4.35 (Table 4-3). The net effect of this would be greater sorption of P in Wauchula compared to EauGallie at a given pH.

Specific adsorption of P occurs by ligand exchange primarily with the aquo and hydroxo groups (Rajan et al., 1974). Ligand exchange of P with aquo groups would add negative charge to the surface but would not increase the concentration of the hydroxyl ions in solution (Eqn. 4-6). In contrast, the exchange of phosphate with hydroxo groups would not affect the surface charge, but would release equivalent amounts of hydroxyl ions in solution (Eqn. 4-7).

$$Al\text{-}H_2O]^{1+} + H_2PO_4^- \rightleftharpoons Al\text{-}H_2PO_4]^0 + H_2O \qquad (4\text{-}6)$$

$$Al\text{-}OH]^0 + H_2PO_4^- \rightleftharpoons Al\text{-}H_2PO_4]^0 + OH^- \qquad (4\text{-}7)$$

The end result of these reactions would be the lowering of the positive surface charge of the oxides in the soil (Table 4-3) and increased competition between hydroxyl and phosphate ions for the specific adsorption sites on mineral surfaces. Addition of P at rates equivalent to 1/2, one, and two times the sorption maximum of the soils, decreased their PZNC values from 3.40 to 3.22 for EauGallie (Fig. 4-10) and from 4.35 to 3.86 for Wauchula (Fig. 4-11), thereby increasing net negative charge in the soil. The increase in

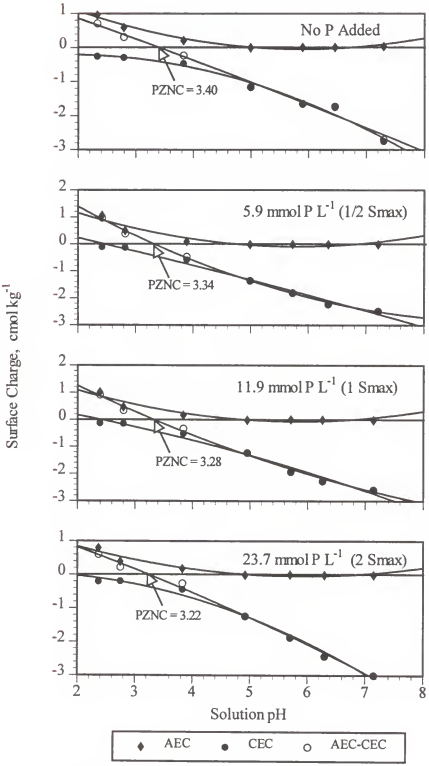



Fig. 4-10. Shifts in PZNC values for EauGallie soil as influenced by P loading. PZNC is point of zero net charge.

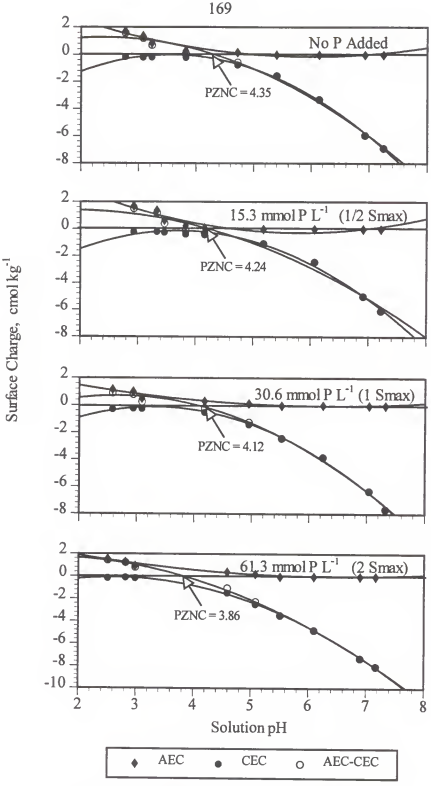



Fig. 4-11. Shifts in PZNC values for Wauchula soil as influenced by P loading. PZNC is point of zero net charge.

negative charge would then oppose further adsorption of P, which would be reflected in the decreasing amounts of P adsorbed with decreasing pH.

There was a positive correlation between Langmuir $S_{max}$ and the binding energy, b ($r=0.654$, $p<0.001$), indicating that at low pH, P was adsorbed mainly on high affinity sites. If sorption of P in the soils did occur by ligand exchange as alluded to earlier, the correlation would suggest formation of inner-sphere complex. According to Sposito (1984), surface complexes resulting from ligand exchange contain no water molecules between the surface Lewis acid site (Al or Fe) and the adsorbed phosphate ion. These complexes are quite stable, showing mainly covalent or ionic bond character.

The desorbability of added P increased with increasing pH. EauGallie exhibited a greater tendency to release P than Wauchula at any given pH. The significant negative correlation of the binding energy with pH ($r=-0.694$, $p<0.001$) and sequentially desorbed P ( $r= -0.479$, $p<0.05$) suggest greater ease of desorbing P at high than at low pH. However, not all of the sorbed P was released into solution with nine 24-h successive extractions. When sequentially desorbed P was expressed as a percentage of initially adsorbed P, Wauchula maintained about 70% of the P in the adsorbed phase. By comparison, EauGallie released about 70% of the initially sorbed P back into solution. The difference in P release properties of the soils could be attributed to the manner with which P was held in the soil. Correlation analyses done separately for each soil indicate that organically bound Al ($CuCl_2$-Al) was mainly responsible for P sorption in EauGallie (Table 4-10). In Wauchula, amorphous Al and Fe oxides (Oxal-Al+Fe) appeared to be the most important contributors to P sorption (Table 4-11). If these relationships indicate

that specific adsorption of P via ligand exchange actually did occur in Wauchula as suggested earlier, and if P in EauGallie was bonded onto organo-metallic complexes, it follows that P would be more "irreversible" in Wauchula than in EauGallie. These findings are in agreement with the recent work of Zhou (1994) who demonstrated that P sorption on metal organic complexes in spodic samples was more "reversible" than that on inorganic metal oxides.

Sorption of P by the spodic samples was characterized by an initially rapid reaction followed by a slower reaction that may continue for a long time without reaching a true equilibrium. The fast reaction in both soils was clearly a function of pH and initial P concentration ($C_o$). The rate of the initial reaction ($k_f$) decreased with an increasing pH at a given $C_o$. The decrease in rate of P sorption with increasing pH could be attributed to the preponderance of surface negative charge at high pH and increased competition between hydroxyl and phosphate ions. An increase in pH would change the electrostatic potential and create more negative charges in the particles, resulting in repulsive forces on the phosphate ions. In EauGallie, the fast reaction was associated with $CuCl_2$-Al ($r=0.652$, $p<0.05$) and KCl-Al ($r=0.971$, $p<0.001$) (Table 4-10) indicating that P in this soil was initially bonded onto Al-organic matter complexes and hydroxy-Al species. In Wauchula, exchangeable Al ($r=0.837$, $p<0.001$) (Table 4-11) was as important as the amorphous Al and Fe ($r=0.723$, $p<0.001$) in determining the rate of the initial reaction. Specific adsorption of P on these mineral surfaces by a ligand exchange was likely the mechanism by which P disappeared at a rather fast rate. Parfitt (1989) attributed the

initial fast reaction of P with various Fe oxides to specific adsorption of P by a ligand exchange mechanism.

The slow reaction of P in the soils was postulated to involve formation of Fe- and Al-P minerals. Based on P fractionation data and the P solubility diagram, initially sorbed P was subsequently transformed into discrete Fe- and Al-P compounds. Both soils were supersaturated with respect to strengite ($FePO_4 \cdot 2H_2O$) (Fig. 4-12; 4-13) and variscite ($AlPO_4 \cdot 2H_2O$) (Fig. 4-14; 4-15) across all pH and P levels. Phosphorus fractionation data further support this theory, as majority of the added P was recovered as Fe/Al-P (Table 4-5).

The fast P desorption reaction in these soils was adequately described by the Elovich equation. The constants $\alpha$ and $\beta$ provide clue to the reaction rates of P release in soils, such that an increase of $\alpha$ and/or decrease of $\beta$ should enhance P desorption.

Phosphorus desorption reaction in both soils was influenced by pH. A significant positive correlation between $\alpha$ and pH in both soils (Table 4-10; 4-11), indicates increased desorption with increasing pH. The rate of P release was also influenced by the amount of initially sorbed P, such that at a given pH, the calculated $\alpha$ values increased. At a given pH and P level, Wauchula exhibited a slower desorption reaction than EauGallie. This implies that P in Wauchula is held more tightly on high energy surfaces than in EauGallie. These surfaces are associated with amorphous inorganic Fe and Al oxides in Wauchula and to the much weaker Al-organic matter complexes in EauGallie.

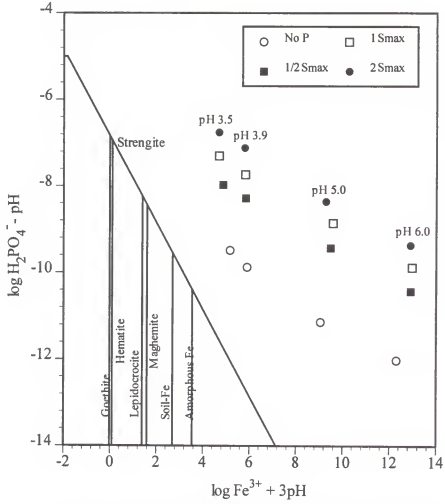



Fig. 4-12. Changes in the solubility of strengite in P-amended EauGallie soil at different pH levels. Points above the line indicate supersaturation with respect to strengite.

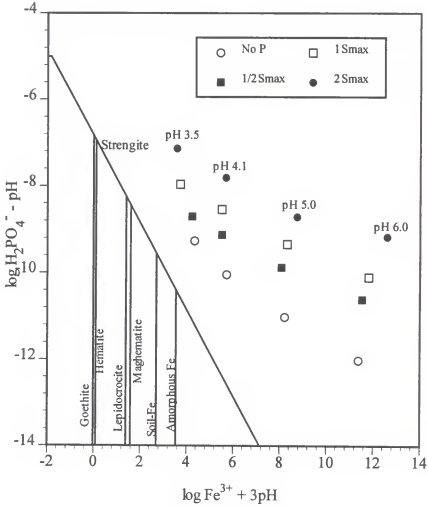



Fig. 4-13. Changes in the solubility of strengite in P-amended Wauchula soil at different pH levels. Points above the line indicate supersaturation with respect to strengite.

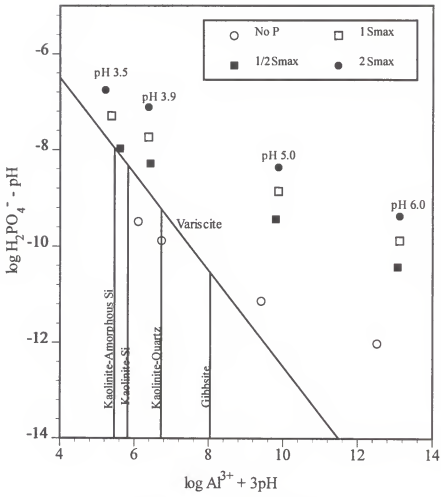



Fig. 4-14. Changes in the solubility of variscite in P-amended EauGallie soil at different pH levels. Points above the line indicate supersaturation with respect to variscite; points below the line indicateundersaturation with respect to the mineral.

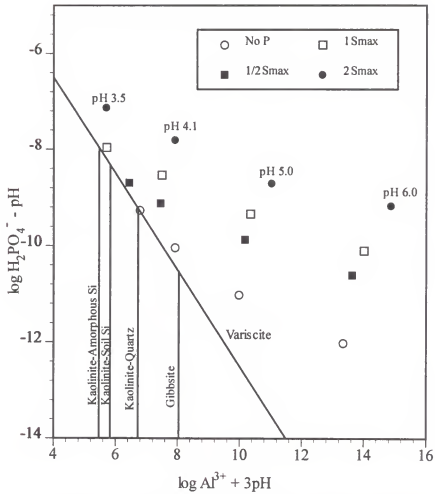



Fig. 4-15. Changes in the solubility of variscite in P-amended Wauchula soil at different pH levels. Points above the line indicate supersaturation with respect to variscite; points below the line indicate undersaturation with respect to the mineral.

Several studies have reported that this short-term type of desorption is a low-activation energy process, one that involves diffusion of the desorbed P through the stagnant water films around the soil particles and within the soil aggregates rather than by chemical reaction (Kuo and Lotse, 1974; Evans and Jurinak, 1976). These authors reported activation energy values of 2 to 3 kcal $mol^{-1}$. Higher activation energies of 20 kcal $mol^{-1}$ reported by Barrow and Shaw (1975) represent the transfer of P between desorbable and fixed forms. Posner and Bowden (1980) suggested that during initial stages of desorption, P held at low activation energies is desorbed. Phosphorus held at higher activation energies is desorbed during the later stages.

## Summary and Conclusions

The spodic horizons showed different affinities for added inorganic P. Under ambient pH conditions, Wauchula sorbed three times more P than did EauGallie. High P sorption capacity of Wauchula was a direct consequence of the high concentrations of Al in this soil.

Manipulation of soil pH altered the P sorption characteristics of the spodic horizons. Phosphorus sorption was high at the low pH range and tended to decrease as the soil became less acid. The reduction in P sorption at high pH was explained on the basis that as pH increases, the surface becomes increasingly negative resulting in greater electrostatic repulsion. This would make reaction with the negatively charged phosphate ions more difficult, thereby reducing sorption. Phosphorus sorption behavior of soils was

better described by the Langmuir than by Freundlich equation. The spodic samples exhibited a hysteretic P sorption behavior that increased with a decrease in pH.

Sorption data were not accurately described by a single first order equation. The occurrence of two distinct slopes on the overall isotherm indicates operation of different reaction mechanisms. Sorption of P by the spodic horizon was characterized by an initially rapid reaction and a slow reaction that may continue for a long time without reaching a true equilibrium. Based on the correlation of the sorption rate constants with the various pools of Al, it was suggested that in the EauGallie spodic, P was initially bonded onto Al-organic matter complexes while in the Wauchula spodic, P reacted initially with the amorphous Al oxides by ligand exchange. The P solubility diagram and the P fractionation data indicate that in both soils, the slow reaction involved subsequent transformation of P into discrete Fe- and Al-P compounds.

The fast P desorption reaction in these soils was adequately described by the Elovich equation. Based on the calculated values of $\alpha$ and $\beta$, desorption of P would be expected to be greater in high-pH soils, as P was held more weakly by the surfaces under this condition. Thus, for a given soil, the potential for environmental pollution from applied P is expected to increase with an increase in pH of the spodic horizon, as has been observed in soils heavily impacted with dairy manure.

# CHAPTER 5
# EFFECTS OF WATER TABLE DEPTH ON PHOSPHORUS LEACHING FROM A DAIRY MANURE-IMPACTED SPODOSOL

## Introduction

Lake Okeechobee is becoming increasingly eutrophic due to excessive phosphorus (P) loading from the surrounding watersheds. The concentration of P in the lake has doubled over the past decade from less than 1.61 to about 3.23 μmol P $L^{-1}$ (Flaig and Reddy, 1995). The bulk of P load to the lake has been traced to the lower Kissimmee River (LKR) and the Taylor Creek/Nubbin Slough (TCNS) basins where dairy farming and beef cattle ranching are the primary land uses (Flaig and Havens, 1995). The LKR basin which supplies 30% of the water input contributed 20% to the total P load, whereas the TCNS basin which provides only 4% of the inflow accounted for 29% of the total P load (Federico et al., 1981). The implementation of Best Management Practices (BMPs) during the last decade has reduced P load from the TCNS basin by 17% (Gunsalus et al., 1992). Currently, the LKR basin provides the greatest P load to the lake (Flaig and Reddy, 1995).

The high soluble P concentrations in the drainage water from these basins have been ascribed to poor management of animal wastes, and unfavorable soil and hydrologic conditions (Allen, 1987). While proper measures have been undertaken to alleviate the problems resulting directly from animal wastes (FDER, 1992), issues related to soils and

hydrology of the area make implementation of effective P control strategies difficult (Allen, 1987). The local climate favors intensive leaching. Lake Okeechobee watershed receives an average of 120 cm rainfall per year with a summer wet season and a winter dry season (McCaffrey et al., 1976). The majority of the soils in the watershed are Spodosols characterized by sandy textures, high infiltration rates, and poor internal drainage due to low permeability of the spodic (Bh) horizon. These conditions give rise to a fluctuating water table that becomes the controlling factor in the transport of P in these soils. Phosphorus retention capacities are generally very low for the A horizon, negligible for the E horizon, and high for the Bh horizon (Mansell, et al., 1995). Thus, any P that moves below the A horizon is generally thought to accumulate in the Bh horizon. However, when the water table is at, or near the soil surface, the movement of P into the Bh horizon is impeded, thus promoting transport of P via surface runoff and lateral seepage to streams and canals through the A and E horizons (Allen, 1988). Dairies located on soils where the water table seasonally rises to the surface have been reported to have higher discharges of soluble P than those located on soils with slight elevation and are not subject to flooding (Allen, 1987).

The solubility of P in soils generally increases upon flooding (Ponnamperuma, 1972; Sanyal and De Datta, 1991). In acid soils, the reduction of free iron oxides during flooding and the liberation of sorbed and coprecipitated P, are considered to be the main source of the increased levels of solution or extractable P (Willett, 1986). The rise in pH that accompanies soil reduction would cause increases in soil solution P by the hydrolysis of aluminum and iron phosphates (Ponnamperuma, 1972; Willett, 1986). Increasing pH

would also tend to reduce the surface positive charge on soils causing desorption of P from clay and aluminum oxide and excess (not yet reduced) Fe (III) oxide surfaces (Tian-ren et al., 1989; Willett, 1989). Such pH changes were, however, found to favor desorption of freshly applied P but not of native P (Willett, 1989). It has been proposed that the pH changes associated with Fe (III) reduction were of greater importance in liberating P than the release of P by reductive dissolution; that is, if P sorbed onto ferric hydrous oxides is a significant source of P in the soil (Willett and Cunningham, 1983; Willett, 1986).

In calcareous soils, the increase in solubility of P is a consequence of the decrease in pH of these soils caused by the accumulation of $CO_2$. The pH is dependent on the partial pressure of $CO_2$ according to the $CaCO_3$-$H_2O$-$CO_2$ equilibrium system rather than on the redox reaction of soils. The solubilities of octacalcium phosphate, β-tricalcium phosphate, hydroxyapatite, and fluorapatite increase with a drop in pH of a flooded calcareous soil (Ponnamperuma, 1985).

Mineralization of organic P was a minor source of P in flooded soils (Patrick and Mahapatra, 1968) except in flooded organic soils (Reddy and Rao, 1983; Uwasawa et al., 1988). Phosphorus mineralization increased with degree of water saturation (Islam and Mandal, 1977) and organic matter content (Willett, 1986). The contribution of organic matter to P release in flooded soils was reported to be mainly through organic P mineralization rather than by promoting reduction of ferric compounds (Uwasawa et al., 1988; Willett, 1989). Organic acids released during anaerobic decomposition of organic matter in flooded rice soils have been reported to decrease fixation of applied P by

forming complexes with soil aluminum and iron (Mandal and Mandal, 1973; Mandal, 1979). Tsutsuki and Ponnamperuma (1987) attributed increased solubilities of Ca-P compounds in flooded soils to the formation of complexes between $Ca^{2+}$ and the decomposition products of organic matter.

The dynamics of native and applied P in soils is influenced strongly by the physico-chemical properties of the soil and by water regimes. An earlier work based on the fractionation scheme of Chang and Jackson (1957) showed that flooding favored the formation of Al-P and Fe-P at the expense of reductant-soluble P (RS-P) in several Louisiana rice soils (Mahapatra and Patrick, 1969). Soils with the greatest amounts of Fe-P had the highest Bray No. 2 (0.1M HCl + 0.03M $NH_4F$)-extractable P indicating that Fe-P was the main source of available P in these soils. In the same study, the authors examined the transformations of Al-P ($AlPO_4 \cdot 2H_2O$), Fe-P ($FePO_4 \cdot 2H_2O$), and Ca-P [$Ca(H_2PO_4)_2 \cdot H_2O$] added to soils at 6.45, 6.45, and 12.9 mmol P $kg^{-1}$, respectively under optimum moisture (field capacity) and flooded conditions. Regardless of the source of P and water condition, the added P was recovered completely in the Al-P and Fe-P fractions. Almost none of the added P was present as Ca-P even where 12.9 mmol P $kg^{-1}$ as [$Ca(H_2PO_4)_2 \cdot H_2O$] was applied. Poor recovery of P as Ca-P was attributed to initially low levels of Ca associated with low pH of the soils. Sah and Mikkelsen (1986a) studied the effects of flooding and draining cycles on inorganic P transformations in alluvial soils. Flooding increased Fe-P at the expense of Al-P fraction. The authors attributed this to the possible transformation of variscite ($AlPO_4 \cdot 2H_2O$) into vivianite [$(Fe_3(PO_4)_2 \cdot 8H_2O$], the most stable Fe-P mineral under reduced condition (Lindsay,

1979). Calcium-P increased during flooding in two soils that had initially high levels of Ca-P but was almost unchanged in two other soils of lower Ca-P content. No significant changes in Ca-P fraction were noted after drainage. The recovery of 3.23 mmol P $kg^{-1}$ added as $[Ca(H_2PO_4)_2 \cdot H_2O]$ was between 69 and 79% in unflooded soils and between 81 and 94% in alternately flooded and drained soils. Applied P was recovered mostly as Al-P in unflooded soils and as Fe-P in flooded-drained soils, indicating that in the soils studied, Al and Fe oxides were the soil components most reactive with P. Conversion of added P in the Ca-P fraction may take place in calcareous soils, but under most noncalcareous flooded soil conditions, applied P was recovered mainly as Al-P and Fe-P regardless of the source of P application (Mahapatra and Patrick, 1969). Sah and Mikkelsen (1986b) also found that the anaerobic decomposition of added organic matter in flooded soils favored the formation of Fe-P and RS-P over Al-P. The authors concluded that the anaerobic decomposition of organic matter enhanced the transformation of crystalline Fe into amorphous forms which led to an increase in Fe-P and severe occlusion of P which, in turn, increased RS-P fraction upon soil drainage.

Studies on P transformations in soils under different moisture conditions are useful in predicting direction of movement and transport of P in the soil. This study was conducted with the following objectives: (i) to contrast the effect of flooding and draining on porewater and leachate pH, electrical conductivity (EC), and soluble reactive phosphorus (SRP) concentrations in Spodosols differentially impacted with animal wastes, (ii) to examine the nature and extent of P transformation and movement in the

soil columns caused by flooding and draining, and (iii) to provide insight on the possible role of the spodic horizon on drainage water quality in the Lake Okeechobee basin.

## Materials and Methods

### Description of Soils

Soils from the intensive and forage components of Dry Lake dairy in Okeechobee, Florida were selected for the study. Intensive areas are those located next to the barn where cattle are held before milking and for some feeding. These areas are generally without vegetation and are heavily impacted with animal wastes. The forage component represents the low-impacted areas, having received small amounts of lagoon effluent and inorganic fertilizers. These areas are used primarily for forage production.

The soil on both sites is mapped as Immokalee fine sand (sandy, siliceous, hyperthermic Arenic Alaquods). This soil has a high permeability in the surface layers (>160 mm $h^{-1}$) and low available water holding capacity (<0.05 mm $H_2O$ $mm^{-1}$ soil depth) (McCollum and Pendleton, 1971). The depth to spodic layer is about 0.89 m with water table normally at a depth of 0.76 m. The depth to seasonal high water table is typically zero to 0.38 m for one to two months, with flooding hazard for two to seven days every one to five years (McCollum and Pendleton, 1971). The Lake Okeechobee watershed receives an annual precipitation of over 120 cm (McCaffrey et al., 1976).

### Collection and Preparation of Columns

Intact soil cores were obtained by hammering Plexiglas tubes (95 cm long, 5.62 cm wide) into the soil to a depth of about 90 cm. The columns included A, E, and Bh

horizons with an average thickness of 21, 60, and 9 cm, respectively. Glass wool was placed between the soil in the columns and bottom rubber stopper to avoid soil loss during leaching. The bottom stopper was fitted with a glass outlet tube connected to a tygon tubing which was used to monitor water depth in the column. The columns were equipped with ceramic cups for porewater sampling, and platinum electrodes for redox measurements (Fig. 5-1). The ceramic cups were pre-washed with 0.1M HCl and rinsed with deionized water to remove P or other active ions. The electrodes, 4 cm long, were placed approximately 3 cm deep into the soil at the center of each horizon and were sealed to the column with silicone glue.

The treatments consisted of two soils in factorial combination with two water treatments and three porewater sample locations. The columns were either flooded or drained to simulate seasonal water table fluctuations. Porewater was sampled below the A (Port 1), the E (Port 2), and Bh horizons (Fig. 5-1). The sample collected at the bottom of the column was the leachate. Soil columns were incubated in a temperature controlled (21°C ± 6°C) greenhouse.

Incubation and Sampling Procedure

Flooded columns. The columns were initially flooded with simulated rainwater (P-free) from below rather than above to avoid leaching of P from the upper layers and to minimize entrapment of air bubbles which would prevent complete soil saturation. The rainwater which was prepared according to Florida rainwater chemistry data contained 17.7, 13.9, 30.7, 9.5, 21.7, 11.7, 18.3, and 1.1 μeq $L^{-1}$ of $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $NH_4^+$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, and $K^+$, respectively. The first porewater samples were taken one week after

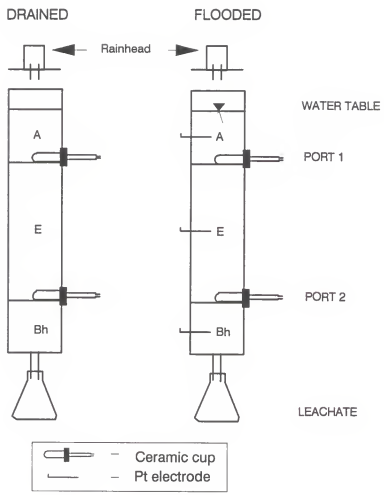



Fig. 5-1. Schematic diagram of the soil columns showing location of sampling ports (ceramic cups) and Pt electrodes.

flooding. Approximately 15 mL samples were taken from each port. After sampling, the columns were allowed to re-equilibrate for a short period after which 5 cm (127 mL) of rainwater were applied to the columns on a weekly schedule for 12 weeks through a "rainhead" consisting of two hypodermic needles that delivered water at a rate of 1.8 cm $h^{-1}$. The water table was restored to its original level by draining the volume of rainwater previously added minus the amount collected via the extraction cups. Moisture loss through evaporation was assumed negligible since the columns were stoppered during incubation, and were open only during application of rainwater.

Drained columns. The columns were kept aerobic throughout the duration of the study. As in flooded columns, rainwater was added on a weekly schedule in the same manner as described above. Following application of rainwater, 15 mL of porewater samples were taken. Suction of 0.1 bar was applied as needed to facilitate porewater sampling. The leachate that drained freely was collected and its volume recorded.

Redox measurements. Readings were taken on two of three replicate columns subjected to the "flooded" treatment. Redox potentials were measured with a portable redox meter and a calomel reference electrode. Addition of +245 mV to these readings corrected redox potentials as measured with a saturated calomel reference electrode to that of a standard hydrogen reference electrode at 25°C (Stumm and Morgan, 1981).

Analytical Methods

Soil. Horizon samples were characterized for various physical and chemical properties prior to the study. Soil bulk density was determined by measuring the oven dry weight of soil present in a core of known volume (Blake and Hartge, 1982). Soil reaction

(pH) was determined potentiometrically using a 1:1 soil:water ratio. Total C and N were measured on finely ground air-dried soil using a Carlo-Erba NA-1500 CNS Analyzer (Haak-Buchler Instruments, Saddlebrook, NJ). Elemental contents were determined by digesting a finely ground sample in nitric-perchloric acid mixture (Olsen and Sommers, 1982). Extracts were analyzed for total P, Ca, Mg, Fe, and Al using an Inductively Coupled Argon Plasma (ICAP) emission spectrophotometer. Phosphorus soluble in water was extracted by shaking 2 g of soil in 20 mL of deionized water for one hour. Mechlich 1 extractable P was determined by shaking 5 g of soil in 20 mL of dilute double acid mixture (0.05M HCl in 0.0125M $H_2SO_4$) for 5 min (Olsen and Sommers, 1982). Phosphorus analysis was done according to the method of Murphy and Riley (1962).

The various pools of Al and Fe in the soils were determined by selective dissolution. Exchangeable Al was extracted with 1M KCl (Barnhisel and Bertsch, 1982). Reactive Al was estimated by extraction with 1M $CuCl_2 \cdot H_2O$ (Juo and Kamprath, 1978). Aluminum and Fe associated with organic matter were extracted with 0.1M $Na_4P_2O_7$ (Wada and Higashi, 1976). Amorphous and crystalline forms of Al and Fe were dissolved in acidified 0.2M $(NH_4)_2C_2O_4$ (McKeague and Day, 1966), and citrate-dithionite-bicarbonate (Mehra and Jackson, 1960), respectively. Aluminum and Fe in the extracts were analyzed using an Inductively Coupled Argon Plasma (ICAP) emission spectrophotometer.

Phosphorus fractionation. Soil P in the columns prior to and at the conclusion of the study was fractionated sequentially into loosely bound P, Al/Fe-P, and Ca-P by single extraction with 1M $NH_4Cl$ (pH 7), 0.1M NaOH, and 0.5M HCl (Hieltjes and Lijklema,

1980). A portion of the NaOH extract was digested to estimate moderately labile organic P (NaOH-$P_o$). Digestion was done in persulfate-sulfuric acid mixture at 380°C (APHA, 1985). Moderately labile organic P was obtained by taking the difference between P in digested and undigested NaOH extract (NaOH-$P_i$). The residue left after HCl extraction was ignited at 550°C for 3 hours and dissolved in 6M HCl solution to obtain highly resistant P referred herein as "residual P". All P determinations were done according to the procedure of Murphy and Riley (1962) using a Technicon Auto Analyzer II.

Phosphorus sorption experiments. Phosphorus sorption characteristics of the spodic horizons were evaluated under aerobic and anaerobic conditions. Phosphorus sorption isotherms for aerobic soils were obtained by shaking duplicate 1-g samples with 20 mL of 0.01M KCl containing P ranging from 0 to 3.223 mM P added as $KH_2PO_4$. For isotherms under anaerobic condition, duplicate 1-g samples in 50-mL centrifuge tubes were suspended in 10 mL of deionized water ($O_2$-free) and incubated for 4 weeks at room temperature. The tubes were kept anaerobic by purging the samples three times a week with pre-purified $N_2$ gas. At the end of incubation, 10 mL of de-aerated 0.02M KCl containing graded series of P solutions were added to the samples, such that the final concentration of P in solution would range from 0 to 3.223 mM P. Equilibration was done in an end-over-end shaker for 24 hours at room temperature. The samples were centrifuged at 3620 *g* for 10 min, filtered through a 0.45 μm filter, and the filtrate acidified with one drop of concentrated $H_2SO_4$. For anaerobic soils, the supernatant liquid was withdrawn with a syringe and filtered under $O_2$-free environment. Phosphorus determinations were done according to the procedure of Murphy and Riley (1962) on a

Technicon Auto Analyzer II. Phosphorus that disappeared from solution after 24-h equilibration was considered to have been sorbed by the soil. Native sorbed P was determined by anion-exchange resin method (Cooperband and Logan, 1994), and was used to correct sorption data according to Fitter and Sutton (1975).

Data were fitted to the linear form of Langmuir and Freundlich equations.

i) Langmuir

$$C/S = 1/bS_{max} + C/S_{max} \qquad (5\text{-}1)$$

where C is the equilibrium P concentration in m$\underline{M}$ P, S is the corrected amount of total P sorbed in mmol P $kg^{-1}$, $S_{max}$ is the adsorption maximum in mmol P $kg^{-1}$, and b is a constant related to the bonding energy in L $mmol^{-1}$ P. The plot of C/S versus C should yield a straight line with intercept and slope equal to $1/bS_{max}$ and $1/S_{max}$, respectively.

ii) Freundlich

$$\log S = \log K + n\log C \qquad (5\text{-}2)$$

where K and n are empirical constants expressed as mmol P $kg^{-1}$ and L $kg^{-1}$, respectively. The plot of logS vs. logC should give a straight line with intercept equal to logK and slope equal to n.

Phosphorus desorption isotherms under aerobic and anaerobic conditions were obtained by subjecting the samples to which 3.223 m$\underline{M}$ P (from sorption study) had been added, to sequential extraction with 20 mL of 0.01$\underline{M}$ KCl equilibrated on a mechanical shaker for 24 hours at room temperature. The samples were centrifuged, filtered through a 0.45 µm filter, and analyzed for P. The same procedure was followed for anaerobic soils except extraction and filtration were done under $O_2$-free conditions. Sequentially

desorbed P was determined by summing the total P desorbed per unit mass of soil after nine successive extractions.

Water. Porewater and leachate samples were divided into two subsamples. The first subsample was immediately analyzed for pH and EC (APHA, 1989). The second subsample was filtered through a 0.45 μm membrane filter, acidified with one drop of concentrated $H_2SO_4$, and analyzed for soluble reactive P using the method of Murphy and Riley (1962) on a Technicon Auto Analyzer II.

Statistical Analyses

General Linear Model (GLM) procedure (SAS, 1985) was used to examine treatment effects on selected chemical porewater and leachate parameters, and on the distribution of the different chemical P forms in the soil. Treatment differences were compared separately for each soil using the Duncan's Multiple Range Test (DMRT). Simple moment correlations were obtained for the water parameters.

## Results

### Soil Characterization

Physico-chemical properties. The soils from forage and intensive components were strikingly different with respect to their initial chemical characteristics. The highly-impacted intensive soil maintained higher pH values throughout the profile than the low-impacted forage soil (Table 5-1). For both soils, pH was highest in the E and lowest in the spodic (Bh) horizon. The presence in the A horizon, of basic cations, particularly calcium in large concentrations accounted for the high pH values. Conversely, the

Table 5-1. Initial chemical and physical properties of the A, E, and Bh horizons of soil cores taken from forage and intensive components of Dry Lake dairy. Values are mean of three replications.

| Property | Forage | | | Intensive | | |
|---|---|---|---|---|---|---|
| | A | E | Bh | A | E | Bh |
| Bulk density, Mg $m^{-3}$ | 1.28 | 1.68 | 1.57 | 1.33 | 1.65 | 1.63 |
| Clay content, g $kg^{-1}$ | ND[¶] | ND | 38 | ND | ND | 14 |
| Total Carbon, g $kg^{-1}$ | 18 | 0.8 | 10.8 | 42.7 | 0.8 | 6.7 |
| pH (1:1, soil/water) | 5.8 | 6.4 | 4.3 | 8.1 | 9.2 | 5.4 |
| Water-soluble P, mmol $kg^{-1}$ | 0.16 | 0.02 | 0.01 | 5.63 | 0.43 | 0.02 |
| Mehlich 1 extractable P, mmol $kg^{-1}$ | 0.32 | 0.04 | 0.12 | 45.88 | 0.49 | 0.41 |
| P fractions, mmol $kg^{-1}$ | | | | | | |
| Labile P | 0.19 (9)[§] | 0.02 (9) | 0.00 (0) | 36.84 (61) | 0.47 (73) | 0.00 (0) |
| Al/Fe-P | 0.21 (10) | 0.03 (12) | 0.19 (42) | 5.28 (9) | 0.06 (9) | 0.51 (56) |
| Organic P | 1.00 (45) | 0.00 (1) | 0.12 (27) | 3.93 (6) | 0.00 (0) | 0.32 (35) |
| Ca/Mg-P | 0.05 (2) | 0.00 (1) | 0.00 (0) | 0.61 (1) | 0.01 (1) | 0.00 (0) |
| Residual P | 0.78 (35) | 0.20 (78) | 0.14 (31) | 14.18 (23) | 0.11 (17) | 0.08 (9) |
| Total phosphorus, mmol $kg^{-1}$ | 2.23 | 0.26 | 0.45 | 60.83 | 0.65 | 0.90 |
| Total calcium, mmol $kg^{-1}$ | 33.73 | 2.8 | 7.49 | 142.58 | 2.73 | 5.55 |
| Total magnesium, mmol $kg^{-1}$ | 3.70 | 0.41 | 1.65 | 62.33 | 0.82 | 1.64 |
| Total aluminum, mmol $kg^{-1}$ | 7.77 | 3.19 | 36.72 | 18.75 | 2.21 | 47.54 |
| Total iron, mmol $kg^{-1}$ | 3.63 | 0.89 | 7.29 | 7.38 | 0.94 | 2.40 |

[¶] ND = not determined.

[§] Numbers in parentheses are percentages of total P.

abundance of Al explained the much lower pH values observed in the Bh horizon. Total elemental concentrations were much greater in the soil from the intensive compared to the soil from the forage component. For both soils, elemental concentrations of P, Ca, Mg, Al, and Fe by horizon was in the order: A >> Bh > E. Bulk density values were higher for the more dense E and Bh horizons (with >95% sand) than the relatively organic carbon-rich A horizon.

Water soluble P (WSP) and Mehlich 1 P (M1-P) concentrations were several fold higher in the intensive than in the forage soil, and tended to decrease with depth. Water soluble P and M1-P in the Bh horizon from both soils represented a fairly small percentage of the total P.

Phosphorus fractions. Phosphorus extracted with 1M $NH_4Cl$ represents P in the labile pool (Pettersson and Istvanovics, 1988; Psenner and Pucsko, 1988). In the A horizon of soil from intensive area, labile P accounted for over 60% of total P. Labile P was very low (< 1 mmol P $kg^{-1}$) in the E horizon, and nonexistent in the Bh horizon (Table 5-1). Phosphorus associated with amorphous and crystalline Al and Fe surfaces ($NaOH\text{-}P_i$) dominated the inorganic P pool in the Bh horizon. The form of P associated with Ca and Mg minerals was extracted with 0.5M HCl. This fraction was generally low, contributing no more than 2% of total in all horizons of both soils. Moderately labile organic P, that fraction of P mainly associated with humic and fulvic acids ($NaOH\text{-}P_o$), was fairly high, accounting for 27 and 35% of total P in the Bh horizon of forage and intensive soils, respectively. Residual P, that portion of P extracted after chemical treatments is considered highly resistant and biologically unavailable (Reddy et al., 1995).

This fraction represented a significant portion of total P in the A horizon of intensive soil (23%). Although this fraction accounted for a high percentage of total P in forage soil, it appears to be of little significance considering the low total P content of the soil.

Forms of Al and Fe. Both elements are concentrated in the Bh horizon (Table 5-2). The soils had far greater Al than Fe. Regardless of form, the levels of Al in both soils were in the order, Bh >> A > E. The same pattern was noted for the distribution of Fe in forage soil but not in intensive soil, where Fe was higher in the A than in the Bh horizon. Aluminum in the Bh horizon was largely amorphous (Oxal). CDB-Al was high but this pool includes both crystalline and noncrystalline forms. Organically bound Al ($CuCl_2$) was also substantial. Exchangeable Al (KCl), which is considered to be the most reactive of the pools accounted for a very small fraction of total Al in the Bh horizon. The distribution of the different forms of Fe in the Bh horizon, percentage-wise, was similar for each soil.

Phosphorus Adsorption-Desorption Parameters

Equilibrium P concentration (EPC). Equilibrium P concentration (EPC) is defined as the solution concentration in which P is neither adsorbed nor desorbed. In theory, it is the solution P concentration at which the amount of P sorbed (uncorrected) intersects the abscissa (x-intercept) in the S versus C plot (McCallister and Logan, 1978). EPC values have been used for predicting direction of P movement in soil/sediment-water systems (Logan and McLean, 1973; McCallister and Logan, 1978).

EPC values obtained for the spodic horizon were generally very low (Table 5-3). Intensive soil had higher EPC values (0.50-1.23 $\mu$M P ) than the forage soil (0.07-

Table 5-2. Forms and distribution by horizon, of extractable aluminum and iron in soils from forage and intensive components of Dry Lake dairy. (KCl is potassium chloride; $CuCl_2$ is cupric chloride; Pyro is sodium pyrophosphate; Oxal is ammonium oxalate; CDB is citrate-dithionite-bicarbonate). Values are mean of three replications.

| Soil | Extractable Al, mmol $kg^{-1}$ | | | | Extractable Fe, mmol $kg^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| | KCl | $CuCl_2$ | Oxal | CDB | Pyro | Oxal | CDB |
| Forage | | | | | | | |
| A | 0.04 (0.5)¶ | 2.04 (26.3) | 1.90 (24.5) | 1.99 (25.6) | 1.93 (53.2) | 2.62 (72.2) | 2.60 (71.6) |
| E | 0.04 (1.3) | 0.94 (29.5) | 0.00 ( 0.0) | 0.35 (11.0) | 0.13 (14.6) | 0.13 (14.6) | 0.44 (49.4) |
| Bh | 2.73 (7.4) | 17.77 (48.4) | 18.44 (50.2) | 23.77 (64.7) | 5.50 (75.4) | 4.80 (65.8) | 6.18 (84.8) |
| Intensive | | | | | | | |
| A | 0.04 (0.2) | 1.90 (10.1) | 1.19 ( 6.3) | 1.86 ( 9.9) | 1.54 (20.9) | 4.42 (59.9) | 4.37 (59.2) |
| E | 0.04 (1.8) | 0.78 (35.3) | 0.00 ( 0.0) | 0.00 ( 0.0) | 0.06 ( 6.4) | 0.04 (4.3) | 0.32 (34.2) |
| Bh | 0.47 (1.0) | 18.76 (39.5) | 20.75 (43.6) | 24.20 (50.9) | 0.56 (23.3) | 0.47 (1.0) | 0.66 (27.5) |

¶ Numbers in parentheses are extractable Al/Fe expressed as percent of total Al/Fe.

Table 5-3. Phosphorus adsorption-desorption properties of the spodic horizon of soils from forage and intensive components. EPC is equilibrium P concentration; $S_{max}$ is Langmuir adsorption maximum; b is Langmuir constant related to adsorption energy; MBC is maximum buffer capacity; K and n are Freundlich constants.

| Parameter | Aerobic | | Anaerobic | |
|---|---|---|---|---|
| | Forage | Intensive | Forage | Intensive |
| EPC, μMP | 0.11 | 1.23 | 0.07 | 0.50 |
| *Langmuir* | | | | |
| $S_{max}$, mmol P $kg^{-1}$ | 5.59 | 3.65 | 4.52 | 4.26 |
| b, L mmol $P^{-1}$ | 15.53 | 14.38 | 25.85 | 12.31 |
| MBC, L $kg^{-1}$ | 87 | 52 | 117 | 52 |
| *Freundlich* | | | | |
| K, mmol P $kg^{-1}$ | 6.90 | 4.01 | 5.67 | 5.00 |
| n, L $kg^{-1}$ | 0.52 | 0.47 | 0.44 | 0.53 |
| P desorbed, mmol $kg^{-1}$ | 5.33 (86)¶ | 3.97 (95) | 5.13 (71) | 3.62 (76) |

¶Numbers in parentheses are P desorbed expressed as percent of initially adsorbed P.

0.11μM P). Based on these numbers, greater sorption of P is predicted to occur in forage than in intensive soil under aerobic and anaerobic conditions. Flooding decreased the EPC values of both soils by as much as 50%. Sorption of added P is expected to be higher under anaerobic than aerobic conditions.

Phosphorus sorption characteristics of the spodic horizons. Under aerobic and anaerobic conditions, the forage soil sorbed more P than the intensive soil (Fig. 5-2). The P sorption capacities ($S_{max}$) of the soils concurred with their respective EPC values except for forage soil under anaerobic conditions. Forage soil sorbed more P than the intensive soil under aerobic (5.59 vs. 3.65 mmol P $kg^{-1}$) and anaerobic (4.52 vs. 4.26 mmol P $kg^{-1}$) conditions (Table 5-3). While flooding increased P sorption in intensive soil, it resulted in a decrease in P sorption in forage soil.

The soils were characterized by comparatively low P-binding energies. The binding energy constants, b, ranged from 12.31 to 25.85 L $mmol^{-1}$ P. Binding energy constants were found to increase with Al (Rajan and Perrott, 1975) and iron oxide contents (Holford et al., 1990). Soils with sorption sites well saturated with native labile P had low b values (Agbenin and Tiessen, 1994).

The maximum P buffer capacity (MBC) of the soil system, which is the increase in sorbed P per unit increase in final solution P concentration, was calculated by the product of Langmuir constants, $S_{max}$ and b (Laverdiere and Karam, 1984). Theoretically, it is the ability of P concentration in the soil solution to resist change when P is added to or removed from the soil (Holford, 1979). MBC values for the soils ranged from 52 to 117 L $kg^{-1}$ (Table 5-3). These values were low compared to the values obtained for

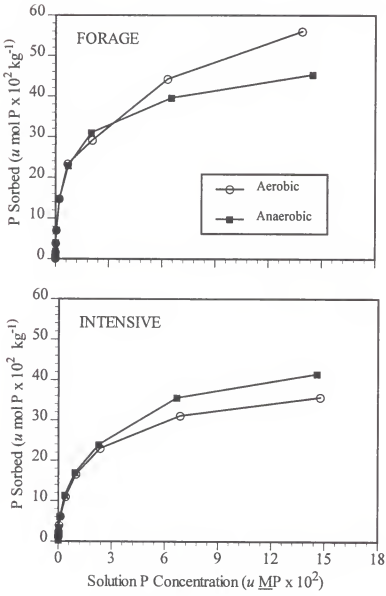



Fig. 5-2. Phosphorus sorption isotherms for the spodic horizon (Bh) of soil from forage and intensive components under aerobic and anaerobic conditions. (Corrected for native sorbed P using resin P values).

podzolic samples from Canada (Laverdiere and Karam , 1984) but were within the range of values reported for semiarid soils of Brazil (Agbenin and Tiessen, 1994).

The Freundlich parameters K and n were similar for the two soils (Table 5-3). There was a good agreement between the K and $S_{max}$. The constant K has been used as a measure of relative P sorption capacity of soils (Biggar and Cheung, 1973; Sanyal and De Datta, 1993; Zhou, 1994). The constant n which has been used synonymously to Langmuir constant b, was found to be closely related to exchangeable Al in acid soils and exchangeable Ca in neutral and calcareous soils (Fitter and Sutton, 1975).

Desorption potential. The soils showed high desorption potentials (Fig. 5-3). Desorption was highest for both soils under aerobic conditions where almost 50% of the P initially sorbed was released back into solution during the first extraction (Fig. 5-3). With nine successive 24-h extractions, desorption of P in aerobic soils was almost complete (86-95%). Under anaerobic conditions, desorption of P by the soils was lower--releasing between 71 and 76% of the initially sorbed P.

Soil Redox Potential

Redox potential ($E_h$) is a quantitative measure of the relative tendency of a given system to oxidize or reduce susceptible components (Ponnamperuma, 1972). It is an indicator of the degree of anaerobiosis in a soil. Redox potentials of >300 mV reflect aerobic conditions while values <300 mV generally indicate anaerobic conditions (Ponnamperuma, 1972).

Redox potential values were quite variable (Fig. 5-4). The soil from the forage site sustained aerobic conditions (+300 mV) in the A and E horizons throughout the

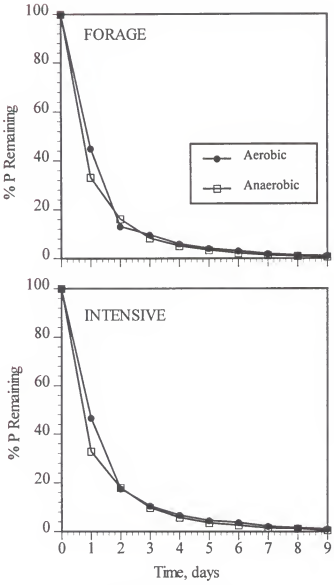



Fig. 5-3. Desorbability of P in the spodic horizon of soils from forage and intensive components under aerobic and anaerobic conditions.

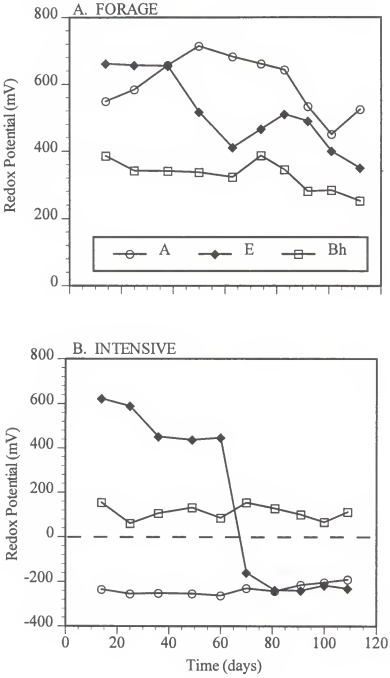



Fig. 5-4. Changes in redox profile of flooded forage (A) and intensive (B) soil columns with time. The points on the graph are average of two readings.

duration of the study. The Bh horizon did not show signs of reduction until about 9 weeks after flooding when the reading fell to about +250 mV. On the contrary, the soil from intensive area reached reducing levels (-200 mV) in the A horizon just two weeks after flooding. Similar values were observed in the E horizon six weeks after flooding. The Bh horizon maintained lower and less variable readings ranging from 0 to +200 mV, than the Bh horizon of soil from the forage site.

The differences in redox behavior between the two soils can be attributed to differences in C content (Table 5-1). Microbial respiration is the primary electron consuming process in these soils, thus, the soil with the higher amount of organic C i.e., intensive area, became anaerobic more rapidly than the soil from the forage area. This was reflected in the A and E horizons but not in the Bh horizon. Soluble organic C from the manure apparently did not leach to the Bh horizon sufficiently enough to effect drastic changes in redox potential. According to Ponnamperuma (1972), soils that are low in organic matter (<15 g $kg^{-1}$) would maintain positive potentials even six months after submergence.

Dynamics of Porewater EC, pH, and SRP

Electrical conductivity (EC). One chemical consequence of flooding is the increase in ionic strength of the soil solution. The increase in ionic strength is due to the release of $Fe^{2+}$ and $Mn^{2+}$ from the reduction of Fe (III) and Mn (IV) compounds, the accumulation of $NH_4^+$, $HCO_3^-$, and $RCOO^-$, and in calcareous soils, the dissolution of $CaCO_3$ by $CO_2$ and organic acids which causes desorption of exchangeable cations

i.e., $Ca^{2+}$, $Mg^{2+}$ (Ponnamperuma, 1972). The relationship between ionic strength (I) and electrical conductivity (EC) is given by the equation

$$I = 0.013\ EC$$

where I is in moles $L^{-1}$ and EC is in mmhos $cm^{-1}$ (Griffin and Jurinak, 1973).

The kinetics of electrical conductivity varied with the water treatment but not with the soil (Fig. 5-5; 5-6). While forage soil maintained much lower EC values than the intensive soil, the general effect of flooding and draining separately for each soil was similar. Under drained conditions, EC showed a generally decreasing trend. Although the values were quite variable initially with respect to sample location, the soils supported stable EC values from ninth week onwards. Mean EC values for forage and intensive soils at three sample locations (Port 1, Port 2, and Leachate) were not significantly different (Table 5-4). Under flooded conditions, EC showed a more distinct pattern. The gradual decline in EC in the A horizon was accompanied by a parallel increase in the E and Bh horizons. Mean EC values were significantly different and of the order Port 1 > Port 2 > Leachate (Table 5-4).

Solution pH. Adjustment of soil pH towards neutrality is one of the chemical changes that occur upon flooding. Changes in solution pH over time were small, and were reflective of the initial pH of the soils (Fig. 5-7; 5-8). Forage soil maintained lower pH values than the intensive soil. Flooding and draining increased pH of the Bh horizon to levels comparable to those of the A and E horizons. This resulted in mean pH values that were not significantly different (Table 5-4). Mean solution pH ranged from 7.2 to 8.0 for intensive soil and from 6.2 to 6.6 for forage soil.

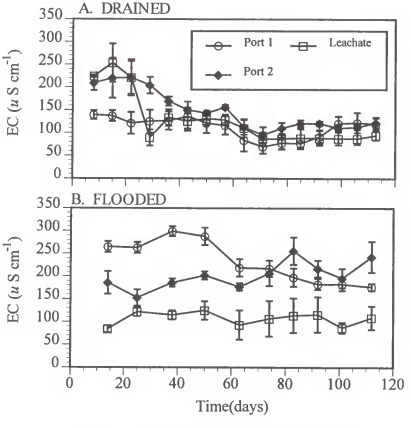



Fig. 5-5. Changes in porewater and leachate EC (electrical conductivity) over time for drained (A) and flooded (B) forage soil columns.

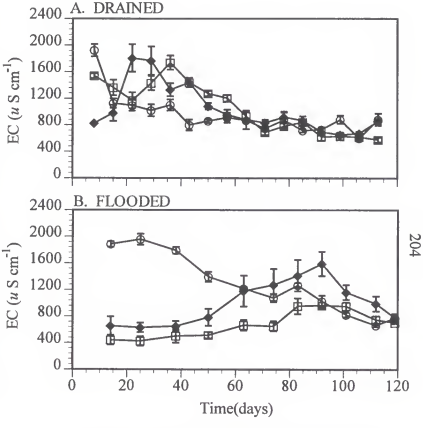



Fig. 5-6. Changes in porewater and leachate EC (electrical conductivity) over time for drained (A) and flooded (B) intensive soil columns.

Table 5-4. Mean porewater and leachate electrical conductivity (EC), pH, and soluble reactive phosphorus (SRP) concentrations for drained and flooded forage and intensive soil columns.

| Sample location | Drained | | | Flooded | | |
|---|---|---|---|---|---|---|
| | EC $\mu S\ cm^{-1}$ | pH | SRP $\mu MP$ | EC $\mu S\ cm^{-1}$ | pH | SRP $\mu MP$ |
| Forage | | | | | | |
| Port 1 (A) | 112*a*[¶] | 6.33*a* | 28*a* | 229*a* | 6.41*a* | 104*a* |
| Port 2 (E) | 149*a* | 6.35*a* | 25*a* | 202*b* | 6.58*a* | 69*b* |
| Leachate (Bh) | 126*a* | 6.17*a* | 3*b* | 117*c* | 6.49*a* | 5*c* |
| Intensive | | | | | | |
| Port 1 (A) | 946*a* | 7.27*b* | 1609*a* | 1170*a* | 7.41*ab* | 1544*a* |
| Port 2 (E) | 992*a* | 7.22*b* | 1802*a* | 1008*b* | 7.35*b* | 1396*a* |
| Leachate (Bh) | 1045*a* | 7.98*a* | 1082*b* | 682*c* | 7.60*a* | 366*b* |

[¶] For a given soil and water treatment, means within a column followed by the same letter are not significantly different at $p<0.05$ by DMRT.

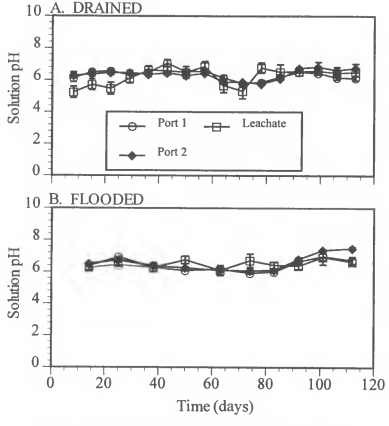



Fig. 5-7. Changes in porewater and leachate pH over time for drained (A) and flooded (B) forage soil columns.

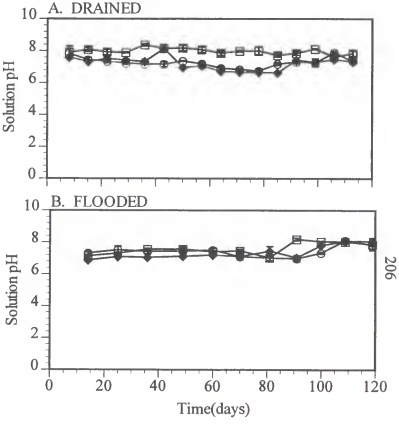



Fig. 5-8. Changes in porewater and leachate pH over time for drained (A) and flooded (B) intensive soil columns.

Soluble reactive phosphorus (SRP). The effects of the water treatments on the dynamics of SRP in the soil columns were quite variable (Fig. 5-9; 5-10). There was no apparent trend in SRP levels at Ports 1 and 2 with time; however, SRP concentrations at these locations were greater than those seen in the leachate. Porewater and leachate SRP levels were several fold higher in soil from the intensive component than in soil from the forage component. There existed a negative correlation between SRP and sample location, meaning SRP concentrations tended to decrease with sampling depth (Table 5-5). SRP concentrations correlated positively with porewater EC and pH of soil from the forage component under flooded and drained conditions, but showed negative correlation only with porewater pH of soil from the intensive area under drained conditions.

To quantify the effects of the water treatments on SRP leaching, the values were averaged over all sampling dates for each of the three sample locations and for each soil (Table 5-4). In both soils, the water treatments resulted in significantly higher levels of SRP in the porewater than in the leachate. In drained intensive columns, mean porewater SRP was about 623 μMP (20 mg $L^{-1}$) higher than leachate SRP. The difference was even greater under flooded conditions--porewater SRP of 1470 μMP compared to leachate SRP of 366 μMP.

Phosphorus Transformations in Drained and Flooded Soils

The nature and extent of P movement in the soil columns were examined by comparing the distribution of the different chemical P fractions in the soil before and after water treatments. There were significant changes in the distribution of P fractions in the soils as a result of flooding and draining particularly in the intensive soil where both

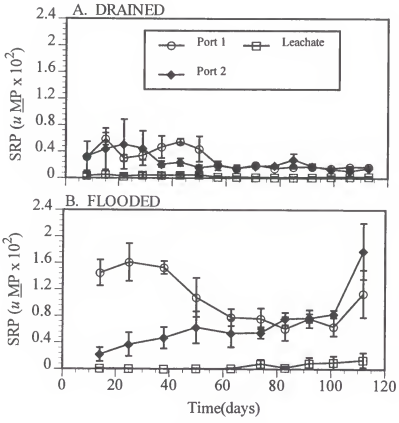



Fig. 5-9. Changes in porewater and leachate SRP concentrations over time for drained (A) and flooded (B) forage soil columns.

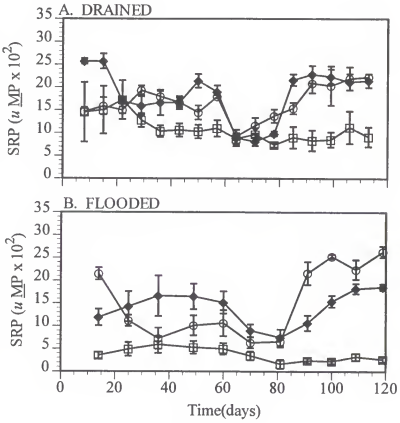



Fig. 5-10. Changes in porewater and leachate SRP concentrations over time for drained (A) and flooded (B) intensive soil columns.

Table 5-5. Correlation of SRP with sample location, EC, and pH for drained and flooded forage and intensive soil columns.

| Parameter | Forage | | Intensive | |
|---|---|---|---|---|
| | Drained (n=143) | Flooded (n=90) | Drained (n=143) | Flooded (n=99) |
| SRP vs. Sample location | -0.437** | -0.709** | -0.378** | -0.629** |
| SRP vs. EC | 0.245** | 0.738** | -0.119 | 0.025 |
| SRP vs. pH | 0.227** | 0.213* | -0.201* | -0.025 |

*, ** Significant at $p<0.05$ and $p<0.01$, respectively.

treatments caused significant leaching of all P fractions except Ca/Mg-P (HCl-P). The labile P ($NH_4Cl$-P) pool appeared to be the most important source of P that leached into the lower horizon. Flooding and draining reduced the labile P fraction in the A horizon by as much as 50% (Table 5-6). Consequently, total P in the spodic horizon increased from ~1 to ~14 mmol P $kg^{-1}$. Although P that moved into the spodic horizon was recovered mostly as Al/Fe-P ($NaOH\text{-}P_i$), a significant portion of the transported P remained in the labile pool. This fraction accounted for over 25 and 28% of the total P in flooded and drained soil columns, respectively. The Ca/Mg-P fraction in the Bh horizon remained low, as this horizon is acidic and contained initially low levels of Ca and Mg (Table 5-1). No apparent changes in the distribution of the various P forms in the E horizon were observed. As alluded to earlier, this horizon is highly eluted having practically no capacity to retain P.

Flooding and draining had similar effects on P transformations in the forage soil. Both treatments resulted in the leaching of labile P into the Bh horizon where it was transformed to Al/Fe-P. Concentrations of the different P fractions were generally very low.

## Discussion

Results of the study demonstrated the effects of flooding and draining on the leaching and transformations of P in a Spodosol differentially impacted with animal wastes. Based on the P data of the soils, the potential for surface water contamination with P was far greater for soil from the intensive than the soil from the forage component.

Table 5-6. Changes in the distribution of the different chemical P fractions in the forage and intensive soil columns following draining and flooding. Values are mean of three replications expressed in mmol P $kg^{-1}$ of soil. (Note: 1 mmol P = 31 mg P).

| Soil | Labile P | | | Fe/Al-P | | | Organic P | | | Ca-P | | | Residual P | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Initial | Drained | Flooded | Initial | Drained | Flooded | Initial | Drained | Flooded | Initial | Drained | Flooded | Initial | Drained | Flooded |
| Forage | | | | | | | | | | | | | | | |
| A | 0.19*a*[§] | 0.06*b* | 0.04*c* | 0.21*a* | 0.24*a* | 0.18*a* | 1.00*a* | 0.59*b* | 0.44*c* | 0.05*b* | 0.07*a* | 0.08*a* | 0.78*c* | 0.98*b* | 1.15*a* |
| E | 0.02*a* | 0.02*a* | 0.02*a* | 0.03*a* | 0.03*a* | 0.04*a* | 0.00*a* | 0.05*a* | 0.05*a* | 0.00*a* | 0.01*a* | 0.00*a* | 0.20*a* | 0.21*a* | 0.21*a* |
| Bh | 0.00*b* | 0.02*a* | 0.01*a* | 0.19*c* | 0.53*b* | 0.64*a* | 0.12*a* | 0.00*b* | 0.01*b* | 0.00*b* | 0.02*a* | 0.02*a* | 0.14*b* | 0.45*a* | 0.40*a* |
| Intensive | | | | | | | | | | | | | | | |
| A | 36.84*a* | 17.64*b* | 18.33*b* | 5.28*a* | 3.03b | 2.46b | 3.93*a* | 1.73*c* | 2.22*b* | 0.61*b* | 1.73*a* | 1.94*a* | 14.18*a* | 4.11*b* | 3.50*b* |
| E | 0.47*a* | 0.49*a* | 0.56*a* | 0.06*a* | 0.07a | 0.08a | 0.00*a* | 0.05*a* | 0.08*a* | 0.01*a* | 0.05*a* | 0.08*a* | 0.11*a* | 0.16*a* | 0.22*a* |
| Bh | 0.00*b* | 3.88*a* | 3.07*a* | 0.51*b* | 8.71a | 8.70a | 0.32*a* | 0.32*a* | 0.13a | 0.00a | 0.32a | 0.13*a* | 0.08*a* | 0.39*a* | 0.30*a* |

[§]For a given soil and P form, means within a row with the same letter are not significantly different at $p<0.05$ by DMRT.

The intensive area had over 60 mmol P $kg^{-1}$ (1860 mg P $kg^{-1}$) in the A horizon compared to only 2 mmol P $kg^{-1}$ (62 mg P $kg^{-1}$) for the forage site. Assuming a bulk density of 1.3 Mg $m^{-3}$ and an average thickness of 20 cm, these figures would translate to 170 and 6 kmol P $ha^{-1}$, respectively. With 60% of the total P in the labile pool, the intensive component would have approximately 102 kmol P $ha^{-1}$ (3160 kg P $ha^{-1}$) in the surface layer that could potentially be available for transport (Table 5-7). Graetz and Nair (1995) reported similar estimates--4000 kg P $ha^{-1}$ for intensive and 1800 kg P $ha^{-1}$ for holding areas.

Weekly monitoring of porewater and leachate SRP concentrations in the soil columns provided evidence for the high P leaching potential of the soil from the intensive component. Chemical fractionation of P in the soils showed that the labile P fraction ($NH_4Cl$-P) was the main source of P that leached into the lower horizons, although contributions from Al/Fe-P and organic P were also substantial. High concentrations of SRP were detected in the porewater early on, indicating rapid movement of P with depth. This was not surprising considering that this soil has a high permeability in the surface layers (>160 mm $h^{-1}$) and a low P retention capacity which does not permit rapid immobilization of heavy loads of P. Spodic horizon can provide storage for P but, like any other soil its capacity to retain P is limited. Thus, the greater the amount of P added to this soil, the greater the potential for loss of P to drainage water.

Significantly higher levels of SRP were found in the leachate of drained than of flooded intensive soil columns (Table 5-8). This was a direct consequence of having more SRP moving with the water under drained conditions which may have resulted from

Table 5-7. Accumulation of chemical P fractions in the forage and intensive soil columns following draining and flooding. Values are mean of three replications expressed in kmol P $ha^{-1}$ $horizon^{-1}$. (Note: 1 kmol P = 31 kg P).

| Soil | Labile P | | | Al/Fe-P | | | Organic P | | | Ca/Mg-P | | | Residual P | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Initial | Drained | Flooded | Initial | Drained | Flooded | Initial | Drained | Flooded | Initial | Drained | Flooded | Initial | Drained | Flooded |
| Forage | | | | | | | | | | | | | | | |
| A | 0.5*a*[1] | 0.1*b* | 0.1*c* | 0.5*a* | 0.6*a* | 0.5*a* | 2.6*a* | 1.5*b* | 1.1*c* | 0.1*b* | 0.2*a* | 0.2*a* | 2.0*c* | 2.5*b* | 3.0*a* |
| E | 0.2*a* | 0.2*b* | 0.2*a* | 0.3*a* | 0.3*a* | 0.4*a* | 0.0*b* | 0.6*a* | 0.6*a* | 0.0*b* | 0.1*a* | 0.0*ab* | 2.1*a* | 2.2*a* | 2.2*a* |
| Bh | 0.0*a* | 0.0*a* | 0.0*a* | 0.2*b* | 0.6*a* | 0.8*a* | 0.1*a* | 0.0*a* | 0.0*a* | 0.0*a* | 0.0*a* | 0.0*a* | 0.2*b* | 0.5*a* | 0.5*a* |
| Intensive | | | | | | | | | | | | | | | |
| A | 102.4*a* | 49.0*b* | 50.9*b* | 14.7*a* | 8.4*ab* | 6.9*b* | 10.9*a* | 4.8*b* | 6.2*b* | 1.7*b* | 4.8*a* | 5.4*a* | 39.4*a* | 11.4*b* | 9.7*b* |
| E | 4.7*a* | 4.9*a* | 5.6*a* | 0.6*a* | 0.7*a* | 0.8*a* | 0.0*a* | 0.5*a* | 0.8*a* | 0.1*a* | 0.5*a* | 0.8*a* | 1.1*a* | 1.6*a* | 2.2*a* |
| Bh | 0.0*b* | 5.8*a* | 4.6*ab* | 0.8*b* | 12.9*a* | 12.9*a* | 0.5*a* | 0.5*a* | 0.2*a* | 0.0*a* | 0.5*a* | 0.2*a* | 0.1*a* | 0.6*a* | 0.5*a* |

[1] For a given soil and P form, means within a row with the same letter are not significantly different at $p<0.05$ by DMRT.

Table 5-8. Total mass of SRP leached from drained and flooded soil columns over the entire study period. Values are mean of three replications.

| Soil | Drained | Flooded |
|---|---|---|
| Forage | | |
| Rainwater applied, cm | 79 | 49 |
| Total leachate SRP, μmol P $cm^{-1}$ rainwater | 0.07*a*[¶] | 0.12*a* |
| Intensive | | |
| Rainwater applied, cm | 72 | 54 |
| Total leachate SRP, μmol P $cm^{-1}$ rainwater | 26.74*a* | 9.10*b* |

[¶] Within a row means with the same letter are not significantly different at $p<0.05$ by DMRT.

greater mineralization of organic P. With an annual precipitation of 120 cm, a cumulative total of 3.12 and 1.08 mmol P would have leached through the Bh horizon with draining and flooding, respectively. These numbers were expectedly low as they represent the SRP that was not retained by the Bh horizon, assuming that P in the moving water did interact with the Bh horizon. These numbers would be higher in soils where the Bh horizon has many voids or holes through which water may readily move (Haan, 1995).

The Bh horizon of the soil from the intensive component retained more P under flooded than under drained conditions. Several researchers (Khalid et al., 1977; Willett and Higgins, 1978; Holford and Patrick, 1981; Bradley et., 1984; Sah and Mikkelsen, 1989) have attributed increased P sorption upon flooding to increased levels of ammonium oxalate extractable Fe (amorphous Fe) in the soil. Although amorphous Fe in the Bh horizon of the intensive area increased upon flooding, the magnitude of change (from 0.47 to 0.55 mmol Fe $kg^{-1}$) was considered marginal to solely account for the observed increase in P sorption. It appears more likely that the increase in amorphous Al (from ~21 to over 27 mmol Al $kg^{-1}$) may have been responsible for increased P sorption. Since Al is not sensitive to redox changes, the observed increase in amorphous Al may have resulted from pH-induced hydrolysis and polymerization of hydroxy-Al associated with the organic matter. Flooding increased pH of the Bh horizon from 5.4 to ~7.0. Bloom (1981) reported adsorption of P by Al peat that increased in the pH range of 3 to 6. Removal of P from solution was attributed both to the adsorption of complex Al-phosphate cations by the peat and to the precipitation of amorphous Al-hydroxy-

phosphate i.e., $AlH_2PO_4(OH)_2$. Haynes and Swift (1989) found increased sorption of P by Al-peat limed to pH 7.

The vast majority of labile P that leached into the Bh horizon following flooding and draining was transformed into Al/Fe-P. This fraction accounted for about 65% of the total P in the Bh horizon of soil from the intensive component. This is consistent with the high levels of Al and Fe and the acid reaction that characterize the Bh horizon. Phosphorus in the Bh horizon is believed to be sorbed onto oxides and hydrous oxides of Al and Fe. Since organic matter is an important component of the Bh horizon, there exists a possibility that P also may be in association with organo-metal complexes. Appelt et al. (1975) prepared a hydroxyl-Al-humic acid complex that was capable of adsorbing P. Yuan (1960) reported that more than 80% of the P applied to acid sandy soils were recovered as Al and Fe phosphates. Phosphorus added to soils as $AlPO_4 \cdot 2H_2O$, $FePO_4 \cdot 2H_2O$, or $Ca(H_2PO_4)_2 \cdot H_2O$ was recovered almost completely in the Al-P and Fe-P fractions, regardless of whether the soils were incubated under optimum moisture or waterlogged conditions (Mahapatra and Patrick, 1969). These reaction products are considered metastable and with time could change into more stable and less soluble compounds which can contribute little to maintaining soluble P in the Bh horizon.

Whether the Bh horizon is a source of or a sink for P depends on a number of factors. On the basis of the sorption data alone, the Bh horizon under both drained and flooded conditions could act as a sorption sink for P. Sorption maximum values of the soils ranged from 3.65 to 5.59 mmol P $kg^{-1}$. Assuming a bulk density of 1.60 Mg $m^{-3}$ and an average thickness of 10 cm, the Bh horizon would take up between 180 to 280 kg P

$ha^{-1}$. These values are low compared to those reported for acid soils high in clay and sesquioxides. Thus, application of P to these soils in excess of their maximum retention capacity would result in having unacceptable amounts of P in the runoff water.

The ability of the soil to sorb added P is largely related to the saturation of the sorption complex. This means that the soil will sorb additional P depending on the number of sites available for further sorption. The soil from the intensive component which had twice more initial P than the soil from the forage component maintained higher EPC values in the Bh horizon. Thus, if a lagoon or drainage effluent of known SRP concentration is brought in contact with the Bh horizon, more SRP from the effluent will be adsorbed by the soil from the forage than by the soil from intensive component. Similarly, the desorption of P is strongly influenced by the extent of saturation of the sorption complex. Both soils showed high desorption potentials with over 50% of desorbed P coming off during the first extraction. Desorption was slow after the first extraction and tended to level off. The greater ease of desorption at higher saturations arises from the fact that the energy of P sorption decreases with increasing surface coverage.

The stability of Al-P and Fe-P compounds in the Bh horizon is another factor that must be considered. Sorption of P in soils involves an initial rapid reaction followed by a a slower reaction that may continue for years (Barrow and Shaw, 1974). The change in rate of reaction with time was thought to involve a shift in the form of P from amorphous to crystalline forms. Crystalline P compounds are very stable and contribute minimally to the labile P pool. Whether the changing water conditions in the Bh horizon will allow for

these reactions to occur was difficult to predict. Under reducing conditions, solution P is released to solution via reductive dissolution and hydrolysis of Al-P and Fe-P. Phosphorus released could end up in the drainage water or re-sorbed onto highly reactive, short-range order, mixed ferrous-ferric iron complex, in soils high in reducible Fe (Khalid, 1977).

Phosphorus transport in these soils is controlled largely by water table fluctuations. For conditions where water flows vertically through the Bh horizon, the Bh horizon would be expected to act as a sorption sink for P. However, the low permeability in the Bh horizon may cause saturated lateral flow in the overlying E horizon which would tend to circumvent the P sorption capacity of the Bh horizon. The high SRP concentrations maintained by the soil in the porewater above the Bh horizon was an indication that P was likely to leave the system via lateral transport in the presence of shallow water tables.

Spodic (Bh) horizon can function as a sink for or a source of P depending on its physico-chemical properties, the hydrologic conditions, and P loading rates. With a plethora of complex and interacting processes operating simultaneously in the soil, it is difficult to make accurate predictions about the P storage capacities of the Bh horizon.

## Summary and Conclusions

The study demonstrated the potential environmental impacts of P leaching in a manure-impacted Spodosol. Based on the soil and water P data, the soil from the intensive component could pose greater threat to the health of Lake Okeechobee than the

soil from the forage component. The higher levels of porewater and leachate SRP maintained in the intensive soil columns under drained conditions suggest that the movement of P from this soil will likely be greater from rainfall events during the dry season than during the wet season.

The labile P pool ($NH_4Cl$-P) was the most important source of P that leached into the Bh horizon. Although P that moved into the Bh horizon was recovered largely as Al/Fe-P, a significant percentage of P in the Bh horizon remained labile. This fraction is in rapid equilibrium with P in soil solution and is highly mobile.

The Bh horizon from the intensive area retained more P under flooded than under drained conditions, a finding substantiated by results obtained from laboratory determinations of the P sorption capacity of the soil. This was attributed to pH-induced adsorption of P by Al-organo complexes (Bloom, 1981) and to the formation of amorphous Al-hydroxy-phosphates (Veith and Sposito, 1977; Bloom, 1981). The greater contact time between the Bh horizon and the P in the soil columns under continuously flooded conditions may also have played a role.

Several strategies have been proposed to effectively control the levels of P in the drainage water entering Lake Okeechobee. The development and implementation of Best Management Practices (BMPs) (Bottcher et al., 1995) during the last decade has reduced the P coming from the TCNS basin by 17% (Gunsalus et al., 1992). However, additional reductions in P entering the lake from this basin are needed to meet the 90% cutback mandated by the South Florida Water Management District (Rechcigl et al., 1995). Phosphorus is imported into the watershed as feed supplements for the animals and as

inorganic fertilizers for pasture. Thus, controlling these P sources in large measure (without negatively impacting the financial profitability of the farm) should control P transport and, consequently prevent rapid eutrophication of Lake Okeechobee.

# CHAPTER 6
# OVERALL SUMMARY AND CONCLUSIONS

Spodosols are the most extensive soils in Florida. These sandy soils occur in a number of areas experiencing the encroachment of intensive dairy and poultry operations which generate large quantities of wastewater and manure (Rhue et al., 1994). Because of their low P retention capacities, these soils, when used for direct disposal of agricultural wastes could pose a great threat to the health of our lakes and streams. In south Florida, wastewaters from intensive dairy land-uses have contributed heavy loads of P to streams that flow into Lake Okeechobee (Allen, 1987). Consequently, the concentration of P in the lake has doubled over the past decade from less than 1.61 to about 3.23 $\mu$mol P $L^{-1}$ (Flaig and Reddy, 1995).

The long-term use of Spodosols as a medium for waste disposal would depend on the ability of the subsurface horizons i.e., Bh and Bw to effectively assimilate P moving from the surface layers. Although the spodic (Bh) horizon has been shown to exhibit a high P retention capacity, the soil factors and environmental conditions under which the Bh horizon can either retain or supply P to our water systems are not well understood. The research included in this dissertation attempted to provide quantitative information on the role of the Bh horizon in the transport of P in Florida Spodosols. Specific research issues pertaining to P retention and release properties of the Bh samples were addressed

through a series of laboratory studies conducted on sixteen Bh samples covering a wide range of Al and Fe concentrations commonly found in Florida Spodosols.

Since adsorption involves the approach of charged particles to charged surfaces, it was necessary to understand the nature of P-sorbing surfaces in the Bh horizon. Thus, the first questions posed were: what types of surfaces are present in the spodic horizon with which P reacts, and what are the charges on these surfaces? And how is the surface charge influenced by P loading?

The Bh samples were Al-dominated with one exception. Average Al and Fe contents of the soils were 153 and 16 mmol $kg^{-1}$, respectively. Selective dissolution analyses showed that Al and Fe in the Bh horizons were largely oxalate-extractable. This amorphous form of Fe and Al oxides comprised a combined average of over 60% of the total Fe and Al in the Bh samples. Iron and Al associated with organic matter (pyrophosphate and $CuCl_2$-extractable) were also high. The crystalline forms of Fe and Al (CDB-oxalate) accounted for a very small portion of the total Fe and Al.

Results from potentiometric titration and ion adsorption studies indicated that the Bh samples had charge properties similar to constant potential colloids, as both the sign and magnitude of the net charge varied with pH and ionic strength of the soil solution. The pH values at which the net surface charge underwent reversal (PZSE) ranged from 2.90 to 4.20. These values agreed fairly well with those obtained from ion adsorption. The pH values at which there was equal adsorption of cations and anions by the soils (PZNC) ranged from 2.60 to 4.90. Both parameters gave high positive correlation with amorphous and organically bound Al. Although Al oxides along with organic matter

dominated the charge properties, the PZSE values did not coincide with the zero point of titration (ZPT), indicating presence of permanent charge. Under natural conditions, the variable charge in the soils ranged from -4.3 to -37.1 mmol $kg^{-1}$. By comparison, the permanent charge component in the soils ranged from -0.4 to +6.7 mmol $kg^{-1}$. Addition of P to selected Bh samples, lowered their PZC values. Phosphorus loading increased the cation exchange capacity of the Bh samples, thereby increasing their net negative charge.

The second issue pertained to the P storage capacity of the Bh horizons. Thus, the following questions were asked. How much P can the Bh samples retain? Does flooding influence their P sorption and release properties? What soil components account for sorption and desorption of P by the Bh horizons?

The Bh samples exhibited P sorption capacities that were consistent with their Al content. Correlation and regression analyses show that $CuCl_2$-extractable Al (Al associated with organic matter) was the single most important chemical property contributing to P retention in these soils although contributions from amorphous and exchangeable pools were also significant. Langmuir $S_{max}$ values for aerobic soils ranged from 3.9 to 30.7 mmol P $kg^{-1}$. Assuming an average thickness of 15 cm, and a bulk density of 1.6 Mg $m^{-3}$ for the spodic horizon, the soils would sorb between 150 and 1170 kg P $ha^{-1}$. These values were typical for Florida Bh samples (Rhue et al., 1994; Zhou, 1994; Nair et al., 1997), but were much lower than the average sorption capacity of over 3000 kg P $ha^{-1}$ estimated for Bh samples from Canada and northeastern United States (Laverdiere, 1982; Yuan and Lavkulich, 1994).

Flooding altered the P sorption and release properties of the Bh samples. The effect, however, was generally small and inconsistent. Flooding reduced P sorption by low-Al soils and slightly increased that of high-Al soils. Because most of the changes in reactivity of P in flooded soils are associated with changes in Fe chemistry, flooding would be expected to produce minimal effects in soils generally low in reducible Fe. The Bh samples studied had an average of 3.6 mmol $kg^{-1}$ oxalate-extractable Fe.

The Bh samples exhibited varying degrees of P sorption-desorption hysteresis. The observed "irreversibility" was most pronounced in high-Al samples, where over 70% of the added P remained sorbed after nine 24-h extractions. The irreversibility of sorption-desorption reactions was thought to involve a shift in the form of P held at the surface from a loosely bound to a more tightly bound type.

Controversy exists in the literature whether or not liming decreases P sorption. Increasing pH has been shown to increase, decrease or not change sorption of P by the soil. Spodic horizons are naturally acidic. However, elevated pH levels have been reported in areas under intensive dairy land-uses. Thus, the following questions were raised. Is the capacity of the Bh samples to sorb P influenced by changes in pH? Does the rate of P sorption and desorption reactions vary with pH? What reaction mechanisms control P sorption and desorption in the Bh horizon?

Results for two Bh samples with contrasting Al contents show decreased P sorption with increasing pH. Phosphorus sorption at any given pH, was greater for high-Al (Wauchula) than low-Al (EauGallie) soil. Correlation and regression analyses indicate that P was sorbed mainly by reaction with Al oxides. The effect of pH on P sorption can

be explained on the basis that as pH increases, the surface becomes increasingly negative resulting in greater electrostatic repulsion. As pointed out earlier, metal oxyhydroxides are amphoteric, that is, they can have a net positive, net negative or net zero charge depending on pH and ionic strength of the ambient solution. The pH value at which the net surface charge is zero is called the point of zero charge (PZC). This condition was established at pH 3.40 for EauGallie and at pH 4.35 for Wauchula. Therefore, at pH values lower than their respective PZCs, the net charge on these soils would be positive, while at pH values greater than the PZC, their net surface charge would be negative. This explains the steady increase in negative charge of the soils as pH increased from 3.5 to 6.0.

The relation between pH and electrostatic potential in the plane of adsorption is another factor influencing the effect of pH on P sorption. As the pH is increased, the charge on the amphoteric surfaces and their electrostatic potential decrease. This would make the reaction with the negatively charged P more difficult and a decrease in sorption should be noted. The effect of pH on electrostatic potential is given by the Nernst type equation:

$$\psi_o = 59\ (pH_{PZC}\text{-}pH)\ mV\ at\ 25\,^{\circ}C$$

Applying this equation to the test soils, with increasing pH, surface potential decreased from -5.9 to -153.4 mV for EauGallie and from +50.2 to -97.4 mV for Wauchula. At a given pH, surface potential for EauGallie soil was lower (less positive) than Wauchula. This is another explanation why P sorption was much larger in Wauchula than in EauGallie.

The ability of the Bh samples to release freshly added P increased with increasing pH. EauGallie exhibited a greater tendency to desorb P than Wauchula at any given pH. The significant negative correlation of the binding energy with pH ($r=-0.694$, $p<0.001$) and sequentially desorbed P ($r=-0.479$, $p<0.05$) suggests greater ease of releasing P at high than at low pH. Leal and Velloso (1973) showed that a significant proportion of the P sorbed at pH 4 was released when the pH was increased to 7 in the Oxisols of Brazil. This type of behavior is generally attributed to the lower bonding energy between sorbed P and oxide surfaces as their negative charge increases with increasing pH.

Sorption of P by the Bh samples was characterized by an initial rapid reaction followed by a slower reaction that may continue for a long time without reaching a true equilibrium. The rate of fast and slow reactions were both influenced by pH and initial P concentrations ($C_o$). The decrease in rate of P sorption with increasing pH and $C_o$ was attributed to the preponderance of surface negative charge at high pH and increased competition between hydroxyl and phosphate ions for the specific adsorption sites on mineral surfaces. The fast reaction was attributed to specific adsorption of P by ligand exchange mechanism primarily on Al oxide surfaces. The slow reaction, based on P solubility and fractionation data was postulated to involve formation of discrete Fe- and Al-P compounds.

Phosphorus desorption reaction in both soils was influenced by pH. A significant positive correlation between Elovich constant $\alpha$ and pH indicates increased desorption with increasing pH. The rate of P release was also influenced by the amount of initially adsorbed P, such that at a given pH, the calculated $\alpha$ values increased. The rapid release

of P at high pH is generally attributed to the preponderance of negative surface charge that weakens the bonding energy between sorbed P and oxide surfaces.

The last key issue addressed in this study dealt with the effect of water table manipulations on P leaching from a Spodosol loaded with dairy manure P. The significance of this study lies in the fact that the majority of Florida Spodosols, especially those belonging to the great group Alaquods, are subject to saturated soil conditions. During the wet summer months, the water table is near the soil surface and becomes the controlling factor in the transport of P in these soils.

Maintaining the water table above (flooded) or below (drained) the Bh horizon resulted in substantial movement of P in the soil columns. High potential for surface water contamination with P was associated with the Spodosol from high manure-impacted areas (also referred to as intensive area/component). Assuming a bulk density of 1.3 Mg $m^{-3}$ and average thickness of 20 cm, with 60% of the total P in the labile pool, the intensive component would have about 3160 kg P $ha^{-1}$ in the surface horizon that could potentially be available for transport. The intensive soil columns maintained high concentrations of soluble reactive P in the porewater above the Bh layer during the entire course of the study. This indicates lack of P sorption in the overlying horizons and greater incidence of P moving laterally above the Bh horizon.

Phosphorus that leached from the surface layer accumulated in the Bh horizon. Under flooded and drained conditions, the soils sorbed between 3.65 and 5.59 mmol P $kg^{-1}$. Using the estimated bulk density of 1.6 Mg $m^{-3}$ and average thickness of 10 cm for the Bh horizon, the soils would take up between 180 to 280 kg P $ha^{-1}$. These numbers

represent between 6 to 9% of the total potentially leachable P. This means that over 90% of the P in the labile pool could end up in the drainage ways by horizontal movement along the eluted E horizon and by downward water movement in some locations where Bh horizons have voids or holes through which water may readily move.

Phosphorus that accumulated in the Bh horizon was found largely in the form of Fe/Al-P. This fraction accounted for about 65% of the total P in the Bh horizon. Most initial precipitates of Fe and Al phosphates are amorphous and may show solubilities that are 10 to 100 times greater than their crystalline counterparts (Haynes, 1982). X-ray amorphous aluminum phosphates have exhibited stability under a pH range of 2.5 to 8.5 (Veith, 1978; Veith and Sposito, 1977). Initial reaction products between P and Fe and Al are considered metastable and with time could transform into more stable and less soluble compounds which would contribute little to maintaining soluble P in the Bh horizon.

This brings us to the final question: is the Bh horizon a source of or a sink for P? On the basis of the P sorption data alone, the Bh horizons under aerobic and anaerobic conditions could act as sorption sinks for P. Their sorption capacities, however were quite variable and depended largely on their Al content. In general, where Al is high, P sorption is high. Langmuir sorption maximum values ranged from as low as 2.4 to 33.7 mmol P $kg^{-1}$ for the Bh samples. Therefore, the risk of P leaching and associated environmental problems are expected to vary from soil to soil. Application of P to these soils in excess of their maximum retention capacity would result in having environmentally unacceptable levels of P in the drainage water. That is why it is

important that the P carrying capacity of the soil is known before using it for any type of waste disposal.

The ability of the Bh horizon to sorb added P is directly related to its initial P content. This means that the Bh samples will sorb additional P depending on the number of sites available for further sorption. For example, Cornelia and Leon fine sands are two soils with similar Al but different native P contents. Leon with 33 mmol $kg^{-1}$ less P sorbed twice more P than Cornelia.

Similarly, the desorption of P is strongly influenced by the extent of saturation of the sorption complex. Regardless of the amount of Al in the Bh horizon, soils with initially high P exhibited great tendency to release freshly added P. This is exemplified by Ona fine sand where release of newly sorbed P was complete after four 24-h sequential desorptions. The desorbability of P in the Bh horizons also appeared to be a function of their Al content. Irrespective of the amount initially sorbed, desorption of P was highest for low-Al soils. Desorption of P by these soils was almost complete after nine extractions. By comparison, the high-Al soils released just over 25% of the sorbed P during the entire duration of the desorption study.

The P sorption and release properties of the Bh horizons are greatly influenced by changes in pH. And these are directly related to the net surface charge of the soils. In general, the higher the pH, the more negatively charged the soil becomes. The soil under this condition would sorb less P that is readily desorbable. The changes in surface charge as a function of pH are intimately associated with the amount of Al and Fe oxides in the soil. Because these minerals remain positively charged at a relatively high pH (7-9), their

net effect would be to increase the amount of positive charge in the soil. Under acid conditions, the oxide surfaces are protonated to yield Al-$OH_2^+$ and Fe-$OH_2^+$. Therefore, the more oxides there are in the soil, the more positive the soil becomes, the greater the sorption of P will be. Phosphorus sorbed at high pH is readily desorbable. As mentioned earlier, this is due to the lower bonding energy between sorbed P and oxide surfaces which become increasingly negative as pH increases. Thus, in areas where heavy manure application has caused pH in the Bh horizon to rise, transport of P in these soils will be higher compared to native, unimpacted soils.

The stability of the reaction products in the Bh horizon is another factor that must be considered. Sorption of P in these soils involved an initial rapid reaction followed by a slower reaction that may continue for some time. The fast reaction was thought to involve specific adsorption of P by ligand exchange while the slow reaction was suggested to involve formation of discrete Fe and Al phosphate compounds. Crystalline P compounds are very stable and contribute minimally to the labile P pool. However, the changing water conditions in the Bh horizon could alter the equilibrium between solution P and solid phase P. Under flooded conditions, low-Al soils supported higher levels of soluble P in the porewater, suggesting possible release of P from reductive dissolution of Fe- and Al-P. Phosphorus released could end up in the drainage ways or re-sorbed onto highly reactive, short-range order, mixed ferrous-ferric iron complex. Since the spodic horizons from Florida are generally low in Fe, this type of sorption regeneration is unlikely to take place. Sorption of P by Al-organic matter complexes has been shown to increase upon drying of the soils (Haynes and Swift, 1989)

The increased P sorption with drying was attributed to the condensation of organic matter which results in increased accessibility of phosphate to adsorption sites on the hydroxy-Al. For spodic horizons that undergo flooding and drying cycles, this could be a possible mechanism by which their P sorption capacities could be enhanced.

Transport of P in the Spodosols is largely controlled by water table fluctuations. For conditions where water flows vertically through the Bh horizon, the Bh horizon would be expected to act as a sink for P. However, the lower permeability in the Bh horizon may cause saturated lateral flow in the overlying E horizon which would tend to circumvent the P sorption capacity of the Bh horizon. The high porewater SRP concentrations maintained by the soil columns from manure-impacted Spodosol during the entire study period was an indication that P was likely to leave the system via lateral transport in the presence of shallow water tables.

Lateral movement of P with water in the soil profile may occur entirely above or below the spodic layer. In some areas where water table intersects the spodic layer, lateral water flow in the soil profile may occur both above and below the spodic layer. On a macro scale, the spodic layer is generally parallel to the soil surface but locally varies in depth (Campbell et al., 1995) thus, contributing to the water table being alternately above and below the layer along a flow path of horizontal water movement toward a drainage ditch, channel or stream.

Based on the facts presented, the function of the Bh horizon as a sink for or a source of P would depend on its physico-chemical properties, the hydrologic conditions, and P loading rates. With a plethora of complex and interacting processes operating

simultaneously in the soil, it is difficult to make accurate predictions about the P storage capacities of the Bh horizon. This study however, has yielded some information that can be used in the modeling of P loading rates in runoff and drainage waters for Florida Spodosols.

The following research topics merit future consideration.

(i) there is a need for the development of reagents that will selectively extract specific pools of Fe and Al in the soil. This will allow more meaningful prediction of the P sorption behavior by these components. This study has demonstrated the general lack of selectivity of the extractants currently in use. For example, if $CuCl_2$ and pyrophosphate reagents were specific for Al associated with organic matter, why did pyrophosphate extract far more Al than did $CuCl_2$? The same is true with oxalate and CDB reagents which were developed to extract amorphous and crystalline forms, respectively. In most cases, the extractability of Fe and Al by these reagents was similar. How can this be possible for a system that is dominated by amorphous materials?

(ii) Since Al-organic matter complexes are important contributors to sorption of P by the Bh horizon, their role as a buffering reserve for reactive Al and as agent for P sorption needs more elucidation. Also, in areas where heavy manure applications have resulted in increased pH of the Bh horizon, it will be interesting to investigate the effect of increased pH on the reactivity of Al-organic matter complexes and its contribution to P sorption. The effect of drying on P sorption can have some important implications for P sorption capacity of the Bh horizons that undergo wetting and drying cycles.

(iii) The stability of various P minerals in the Bh horizons from manure-impacted and unimpacted soils deserves careful investigation.

APPENDIX A
NORMALIZING FREUNDLICH K VALUES

The question of whether Freundlich K should be regarded a unitless quantity came up during comparison of K values published in the literature. The Freundlich equation is commonly written as:

$$S = KC^n \qquad \text{(A-1)}$$

where S is the amount of P sorbed, C is the solution P concentration, K is the adsorption coefficient, and n is a constant. In linear form, the equation is written as:

$$\log S = \log K + n\log C \qquad \text{(A-2)}$$

The plot of log S versus log C should give a straight line with a slope equal to n. That is,

$$(\Delta\log S/\Delta\log C) = n \qquad \text{(A-3)}$$

if S has a unit *mmol P* $kg^{-1}$ and C carries a unit equal to *mmol P* $L^{-1}$, it follows that n should have a unit $L\ kg^{-1}$. For the units in equation 2 to be equal on both sides, K should have a unit that is consistent with that of S. A common mistake is to pick out literature values for K and compare it to our own without checking how these values were derived. The numerical value of K would be small if S and C were expressed on a mole basis. Conversely, K would be large if S and C had units expressed on a gram basis. The following is a direct procedure for standardizing K values with respect to S and C.

Case 1. With S and C expressed as *mmol P* $kg^{-1}$, and *mmol P* $L^{-1}$, respectively.

$S \times 31 = S^*$ (mg P $kg^{-1}$); $S = S^*/31$

$C \times 31 = C^*$ (mg P $L^{-1}$); $C = C^*/31$

Substituting the new values for S and C in Eqn. A-1:

$$(S^*/31) = K\,(C^*/31)^n$$

Rearranging the equation:

$$S^* = 31K\,(C^*/31)^n$$

$$S^* = 31K\,(C^{*n}/31^n)$$

$$S^* = (31K/31^n)\,C^{*n}$$

Thus, the new value for K with unit equal to S* would be:

$$K^* = 31K/31^n$$

$$K^*(\text{ mg P kg}^{-1}) = K/(31)^{n-1}$$

Case 2: With S and C expressed in *mg P kg$^{-1}$* and *mg P L$^{-1}$*, respectively.

$$S/31 = S^* \text{ (mmol P kg}^{-1}\text{)};\ S = S^*\,(31)$$

$$C/31 = C^* \text{ (mmol P L}^{-1}\text{)};\ C = C^*\,(31)$$

Substituting the new values for S and C in Eqn. A-1:

$$S^*(31) = K\,[C^*(31)]^n$$

Rearranging the equation:

$$S^*(31) = K\,C^{*n}\,31^n$$

$$S^*(31) = (K31^n)\,C^{*n}$$

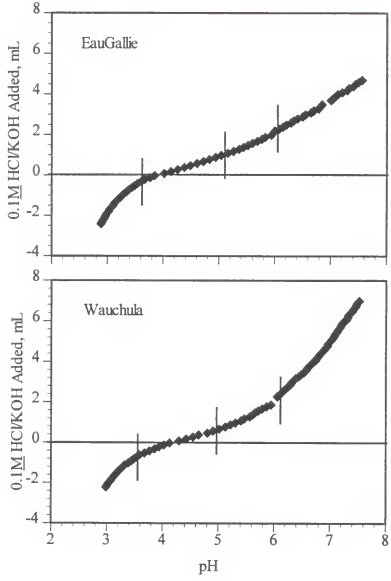
$$S^* = [(31)K31^n)]\,C^{*n}$$

Thus, the new value for K with unit equal to S* would be:

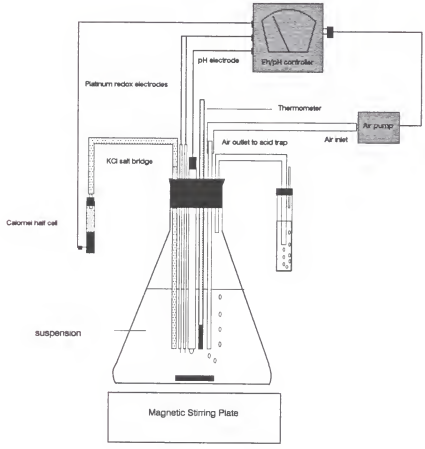
$$K^* \text{ (mmol P kg}^{-1}\text{)} = (31)K31^n$$

Since the value of n does not change with the units of S and C, directly plug this number into the new equation for K* to get the appropriate value.

APPENDIX B
TITRATION CURVES FOR THE SOILS



APPENDIX C
DIAGRAM OF THE SETUP ORIGINALLY PROPOSED FOR P SORPTION-DESORPTION STUDIES



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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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